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16. ABSTRACT

This report concerns the existence, source and fate of chlorinated and nonchlorinated organic compounds in the Lower Fox River of Wisconsin. Raw and treated wastewaters, surface water, seston, snowmelt, sediment, fish and clams were sampled. A total of 105 compounds were identified and an additional 20 compounds were characterized by GC/MS. Twenty identified compounds are on the U.S. EPA Consent Decree Priority Pollutant List. The study shows PCBs and some other chloro-organics in effluents are reduced by efficient suspended solids removal. It is possible, but not proven, that some chloro-organics are formed by process or effluent chlorination. Clams were found to rapidly bioaccumulate PCBs. Fish fillet samples contained PCB concentrations up to 90 mg/kg. Sediments throughout most of the river were found to be contaminated with PCBs. An extensive bibliography is included.

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by

WISCONSIN DEPARTMENT OF NATURAL RESOURCES
WATER QUALITY EVALUATION SECTION

In fulfillment of

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for the

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
Chicago, Illinois 60604

EPA Project Officer: Howard Zar

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ABSTRACT

This study was developed because of the increasing concern over potentially toxic chlorinated and nonchlorinated organic compounds entering the environment. The Lower Fox River was studied because of the large number of industrial and municipal wastewater treatment systems discharging to this 64-kilometer stretch of river. Effluents, surface water, seston, snowmelt, sediment, fish, and clams were sampled.

A total of 105 compounds were identified by gas chromatography/mass spectrometry. An additional 20 compounds were characterized but not conclusively identified. Twenty identified compounds are on the U.S. EPA Consent Decree Priority Pollutant List. The study indicates that PCBs and some other chloro-organic compounds are associated with effluent suspended solids and that solids removal reduces effluent contaminant concentrations.

Effluent concentration ranges in ug/L for compounds quantified by GC/MS were: benzothiazole 10-30, hydroxybenzothiazole 10-30, methyl thiobenzothiazole 10-40, trichloroquaiacols 10-60, tetrachloroguaiacol 10-50, dichlorophenol 15-40, Trichlorophenol 5-100, Tetrachlorophenol 2-20, Pentachlorophenol 5-40, dehydroabietic acid 100-8500, and PCBs 0.4-68.0. It is possible, but not proven, that some compounds were formed by process or effluent chlorination.

Clams were found to rapidly bioaccumulate PCBs. After a 27-28 day exposure, PCB concentrations in clams ranged from 255 to 740 ug/kg. Fish fillet samples contained PCB concentrations up to 90 mg/kg. Sediments throughout most of the river were found to be contaminated with PCBs. Toxicity data are lacking on many of the identified compounds and additional data are needed.

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I. Summary

A total of 105 compounds were identified by gas chromatography/mass spectometry (GC/MS) in selected extracts of wastewater, surface water, sediment, snow,and biological samples. An additional 20 compounds were characterized but not conclusively identified. Twenty of the 105 compounds are on the EPA Consent Decree Priority Pollutant List. Other compounds identified, including chloro-guaiacols, chloro-phenols, resin acids and chloro-resin acids have been reported to be toxic to fish by other investigators of pulp and paper mill wastewaters. Also identified are other wood extractive and lignin-related compounds such as acetovanillone, fatty acids, guaiacol, syringaldehyde, and vanillin. Several identified compounds commonly used in industry are benzothiazole, bisphenol A, and nonyl phenol. Several compounds apparently not previously reported in wastewater are chloroindole, chlorosyringaldehyde,and, tentatively, chloro-bisphenol A's.

Concentrations of the various compounds ranged from 0.5 to 100 ug/L. An exception was dehydroabietic acid (DHA), a toxic resin acid not found on the Priority Pollutant List. It was frequently found in pulp and paper mill effluents in concentrations ranging from 100 to 8500 ug/L.

Sampling data and laboratory experiments show PCBs and some other chloro-organics associated with suspended solids. Suspended solids reduction reduces the chloro-organic concentration from raw to final effluents of both pulp and paper mills and municipal sewage treatment plants receiving pulp and paper mill wastes.

Polychlorinated biphenyls (PCBs) were found in every type of environmental sample collected during this investigation in the Fox River watershed. Two hundred and fifty samples of pulp and paper mill wastewaters, sewage treatment plant wastewaters, river and lake sediment, river water, seston, snowmelt, clams,and fish were examined.

Of the 26 wastewater effluents sampled, 12 contained detectable levels of PCBs. Concentrations of PCBs in final effluents ranged from 0.1 to 56 ug/L while raw wastewaters contained levels from 0.2 to 8200 ug/l. Most effluents containing PCBs were related to paper mills using recycled paper fibers in their production process. Aroclor 1242 was the predominant mixture detected, although 1248 and 1254 were also found.

Levels of PCBs in 16 seston samples averaged 0.016 ug/L of filtered water. The concentration of PCB associated with seston in river water increased as the water traveled downstream and became exposed to more discharge points.

PCBs in Fox River water were detected in 9 out of 25 samples collected. The concentrations ranged from 0.05 to 0.85 ug/L. Samples containing PCBs were collected near the outfalls of sewage treatment plants and pulp and paper mills.

The concentration of PCBs in 34 river bottom sediments ranged from 0.05 to 61.0 mg/kg on a dry weight basis. PCBs were not found in some samples taken from Green Bay or upstream from all known PCB point sources. Sediments with highest PCB concentrations were near known PCB discharge points.

Clams seeded at various locations in the Lower Fox River rapidly accumulated PCBs. After 27-28 days exposure in the Lower Fox River,clams accumulated PCBs from 255 to 740 ug/kg. The amount of PCB bioaccumulation in seeded clams appears to be related to sediment concentrations.

Thirty-five fish samples from two locations contained PCBs. Concentrations varied from 0.5 to 90 mg/kg fillet tissue. The concentration of PCB in all of the sampled species was proportional to fat content. Aroclor 1242 was the predominant PCB mixture detected at the upstream site while 1248 was almost exclusively found downstream. Analytical masking or selective bioaccumulation of the higher chlorinated isomers, which are more lipid soluble, may be responsible for this effect.

II. INTRODUCTION

The current concern with the fate of chlorine in the aquatic environment arises because,for decades, chlorine has been the principal means of disinfecting drinking water and wastewater effluents. More recently, chlorine has achieved importance as an anti-foulant for the cooling systems of power production facilities. Together, these uses consume 3 to 4 percent of the nation's chlorine production (1). Increased understanding of the ecological problems associated with chlorinated pesticides and polychlorinated biphenyls (PCBs) has caused increased concern that other chloro-organics may be formed in the chlorination process and have similar impacts.

The presence of organic compounds in the water supplies of some large U.S. cities has been documented (2,7). The results of a study by the U.S. Environmental Protection Agency (EPA) in 1974 indicated that the drinking water in New Orleans contained 66 organic compounds (3). Since then, EPA has investigated the water supplies of 80 other cities under the National Organics Reconnaissance Survey (NORS). This sampling program indicated the presence of one or more organohalide in 79 of the supplies (4). The occurrence of halogenated (e.g. chlorine) organics in finished water has been demonstrated to be widespread and to be a direct result of the chlorination practice (5).

An even greater potential for chloro-organic formation is present when municipal wastewater is chlorinated, because of its high organic content. When used for disinfection, chlorine was thought to be oxidizing the organic compounds to harmless substances and thereby lowering the biochemical

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oxygen demand of the effluent. Research has now shown that although chlorine does oxidize many substances, it can also create many organochlorine compounds which were not present in the raw wastewater entering the treatment plant (6,42,52,58). The incorporation of chlorine into an organic molecule generally increases its lipophilic character and at the same time increases the toxicity, persistence, and bioaccumulation properties. Measurements that illustrate the nature of chloro-organics are of interest because such information is useful in efforts to regulate these compounds.

Of particular interest in Wisconsin is the chlorine or chlorine-containing compounds being used by pulp and paper mills, one of the major industries of the state. While 3 to 4 percent of the chlorine manufactured in this country is used for wastewater and potable water disinfection, 15-16 percent is utilized by the pulp and paper industry (1). During 1976 the pulp and paper industry in the Lower Fox Valley reported using over 34 metric tons of chlorine per day (100). If chloro-organic compounds are formed in the disinfection of wastewaters, it is reasonable to postulate that similar compounds are created in the pulp and paper bleach process and can gain entry into the open environment. Indeed, several investigators have reported chloro-organics in bleached pulp mill effluent (8, 22-26, 31, 36, 46).

Because of this interest, U.S. EPA (Great Lakes National Program, Region V) contracted with the Wisconsin Department of Natural Resources (DNR) and the associated State Laboratory of Hygiene (SLH) to initiate an explorative study of chloro-organics in the Lower Fox River. The major goals of the study follow:

1. To monitor the distribution and occurrence of PCBs and suspected chloro-organics.

2. To identify previously undetected chloro-organic compounds in Lower Fox River effluents, surface water, biota, and sediment.

3. To determine which methods of treatment would be best suited for chloro-organic removal from wastewater.

4. To describe the fate of PCBs in the Lower Fox River in terms of a mathematical model.

The Lower Fox River is 64 kilometers long and extends from the outlet of Lake Winnebago to Green Bay (Figure 1). The Lower Fox is one of the major drainage streams in Wisconsin and is the most industrialized. It is controlled by 11 dams and is navigable via an extensive series of locks. The mean flow for the water year October '76 to September '77 at the Rapide Croche Dam was 54.35 m^3/s. The average discharge for the 81-year record is 117.7 m^3/s (101). Industrial pollution has been a problem since the early 1900s. Wisconsin DNR water pollution surveys dating back to 1938 indicate BOD, suspended solids, and dissolved oxygen problems. Numerous references to fish kills are also found in Wisconsin DNR fish management files.

Previous investigations indicate PCBs are present in the Lower Fox River (10). This stretch of the river is also likely to contain other chloro-organics since it receives the treated discharge from 15 pulp and/or paper mills, one electric power plant, and 11 municipal wastewater treatment plants serving a population of over 250,000 people.

The information generated by this study will be used to establish or revise effluent discharge limitations. Under the authority of the Federal Water Pollution Control Act Amendments of 1972, P.L. 92-500, and the 1977 amendments to it, the EPA must establish limitations including toxic compounds for existing sources, standards of performance for new sources, and pretreatment standards for discharge to publicly-owned treatment facilities. The date for promulgating the limitations and standards for the pulp and paper industry is September 30, 1979. Thus, the information developed in this study will be applicable to the Federal pollution control schedule.

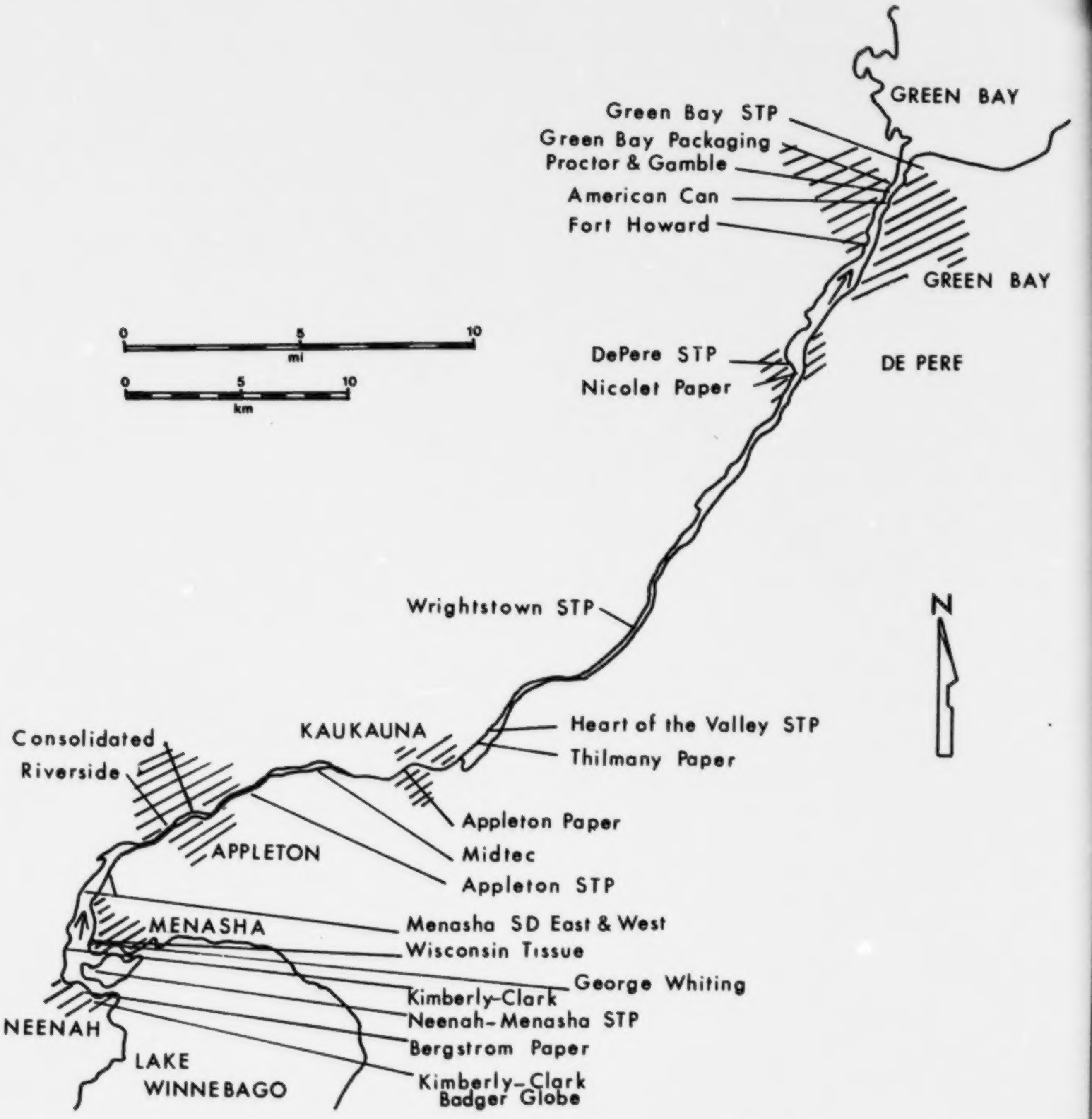
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Figure 1. Municipal and Industrial Waste Discharges to the Lower Fox River.

III. MATERIALS AND METHODS - SAMPLE COLLECTION

EFFLUENT

Sampling was restricted to municipal wastewater treatment plants and pulp and paper mills because of their high chlorine usage. Sampling was performed by plant personnel to facilitate a time-of-travel study. Self-sampling was necessary because of the large number of dischargers and limited number of DNR personnel attached to this project. Detailed sampling instructions were sent to each discharger several weeks in advance, and each one was telephoned just prior to the scheduled sampling date. Cooperation was excellent from all but one discharger.

Twenty-four-hour flow proportional composite samples of influent to and effluent from wastewater treatment systems were collected when possible. If composites were not available, grab samples were taken. Samples were refrigerated until picked up by DNR personnel within 24 hours of collection. They were placed in coolers and hand-delivered to the laboratory within 48 hours of removal from the waste stream. Glass bottles (2.5 L) washed with detergent, hot water, acid,and distilled water were supplied by DNR. All bottle caps were lined with aluminum foil.

SURFACE WATER

River and lake water samples were collected within 0.5 meter of the surface at all locations. When samples were taken from piers, dams, or bridges, a metal bucket was lowered by rope to make the collection. The

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water sample was poured into the sample container, which was rinsed at least twice with the water sample before the actual sample was collected. When samples were taken from a boat, the sample bottle itself was dipped into the water. Care was taken to avoid gas and oil contamination from the boat's motor.

These samples ranged in volume from 2 to 10 liters. In all cases they were immediately capped with an aluminum foil-lined top and placed in insulated chests. The samples arrived at the laboratory within 48 hours of collection.

SEDIMENT

The bottom sediment is generally considered the ultimate "sink" for most contaminants reaching the aquatic ecosystem. Polychlorinated biphenyls and other chlorinated organic compounds are associated with particulate matter. It is assumed that most particulate matter settles out in slow current areas, carrying these compounds to the bottom of the river. Compounds in sediment may be redistributed via biological activity, oxidation reduction reactions, volatization, physical disturbance, etc.

Twenty sediment samples were collected from Lake Winnebago to Green Bay. An additional 14 sediment samples were collected in the lower part of Green Bay to help establish the distribution of organic contaminants. Sampling sites were located in conjunction with point sources, obvious sediment build-up areas, and the prevailing current in Green Bay.

Sediment was collected with a Peterson Dredge at all sites. Upon retrieval, the dredge was opened upside down and the sediment was scooped out of both sides of the dredge with a quart-sized wide-mouth mason jar. The jars had been previously rinsed with hexane, and lids were covered with aluminum foil. All samples were then transported to the laboratory within 48 hours. Samples that could not be processed immediately were frozen.

CLAMS

The concentration of chloro-organic compounds at any one point in a flowing river is in a continuous state of flux due to discharge variations. Therefore, grab samples of the water column may not result in a completely accurate determination of compounds present in the ecosystem.

Freshwater clams filter feed on plankton and organic detritus. When clams are feeding, a continuous stream of water passes through them, and suspended particles are directed to the mouth after being filtered by the gills. It has been established that clams bioaccumulate chemical compounds in solution (9), and tissue concentrations eventually reach an equilibrium that is correlated with the concentration in the water. Very few clams are naturally present in the Fox River; therefore clams were "seeded" at strategic locations as a biomonitoring organism.

Clams (Anodontoides ferussacianus)* were collected from the Deerskin River, Vilas County, Wisconsin, which is devoid of point sources of chlorinated compounds. Three specimens were sacrificed and screened for chlorinated organic compounds by GC/EC analysis, and no contaminants were detected. Immediately after collection the clams were transported in ice chests containing water from the collection stream and were placed in the Fox River.

---

* Identification by Harold A. Mathiak, Horicon, Wisconsin

The clams were secured at the sampling sites by carefully drilling a small hole in one half of the outer margin of the shell, placing a loop of heavy monofilament line through the hole, and tying a sufficient length of nylon line to the monofilament loop to assure free movement. The nylon line was then secured to various anchors at each site (tree limbs, buoys, etc). Wire baskets were rejected because of the problem of solids or slime accumulation on the baskets and potential smothering of the clams. All clams were gathered from the Deerskin River on May 23, 1977 and were placed in the Fox River by May 25, 1977.

A total of 74 clams were placed at 10 locations and harvested from each site at varying time intervals. Upon collection the clams were wrapped in aluminum foil, placed on ice, and transported to the laboratory for analysis. If the clam's abductor muscle was under tension it was assumed that the specimen was alive and had been filtering for the full time in place. It was recognized that time of submersion is not necessarily equal to clam filtering time.

FISH

The discovery of PCBs in the environment in 1966 prompted investigations of PCB bioaccumulation in fish (10). These studies did indicate that PCBs were bioaccumulating to high concentrations in Fox River fish.

Other investigations have shown that PCBs and other organic compounds may also bioaccumulate in fish (21, 58, 62, 83).

Previous testing has shown that high fat content species such as carp and trout generally contain much higher PCB concentrations than do low fat content fish such as walleye and northern pike (10). It is therefore desirable to include both game and rough fish in a sampling program; rough fish because they are more apt to contain the lipophilic compounds of interest and game fish because they are more likely to be consumed by humans. The species of fish commonly found in the Fox River collected for this study are given in Table 1, along with their predominant feeding habit.

Table 1. Fish Collected and their Feeding Habit.

Common Name	Scientific Name	Feeding Habit
Carp	Cyprinus Carpio	Omnivore
White Sucker	Catostomus Commersoni	Omnivore
Yellow Perch	Perca Flavescens	Planktivore/Predator
Yellow Walleye	Stizostedion Vitreum	Predator
Northern Pike	Esox lucius	Predator

A fyke net was used to collect fish from Little Lake Butte des Morts and below the De Pere Dam in April, 1977. A total of 35 samples were retained for analysis. A sample was composed of either a large single fish or a composite of two or more small fish. Immediately after collection the fish were wrapped in individual aluminum foil packages, placed on ice, and transported to the laboratory for freezing prior to analysis. As laboratory time permitted, the fish were partially thawed, filleted, chopped, and placed in glass containers. All sample bottles were thoroughly cleaned, hexane rinsed, and fitted with aluminum foil-lined caps prior to use.

SNOWMELT

Nineteen snowmelt samples were collected by thawing a sufficient quantity of snow from vertical snow columns to yield 2.5 L of water. Samples were collected by melting snow in a clean metal container,using a portable gas stove as a heat source. Temperature measurements were made on the slush as a precaution against excessive heating and possible chloroorganic loss by vaporization. The sample temperature was maintained at $\leq 25^{\circ}C$ as measured at the slush surface. The water was poured into a glass sample bottle, covered with a metal-lined cap, and placed in insulated chests for transport to the laboratory.

SESTON

Seston includes all suspended matter in a body of water, both living and non-living, which is capable of being removed by filtration. Seston samples were collected because of the presumed absorptive characteristics of suspended material, and the possible bioaccumulation of many compounds by planktonic organisms. If chlorinated organic compounds were present in the river, even in low concentrations, they would likely be found in detectable concentrations in the seston.

Seston samples were collected from 16 stations with a small gasoline engine powered pump. The outlet side of the pump flowed through a calibrated meter to allow determination of the volume of filtered water. The metered flow was directed through a #20 mesh (80 um) plankton net with a #20 mesh cup attached. The body of the net was submerged in water at all times to decrease pressure on the net and loss of material. It was recognized that many small particles, including some of the smaller phytoplankton, may pass through the net. It was standard procedure to pump until a visible amount of material was present in the net. All samples were collected from a depth of one meter. After pumping, the samples were concentrated in the attached cup and transferred to glass bottles. Samples were stored in a Styrofoam container and transported within 48 hours to the laboratory for analysis.

IV. MATERIALS AND METHODS - LABORATORY

EXTRACTION PROCEDURES

A. Water and Wastewater Samples (Figure 2)

Reagents

1. Chloroform, ACS, redistilled in glass.
2. Hexane (Skelly Solve B) b.p. 60-68°C, redistilled in glass.
3. Sodium sulfate, ACS, granular, anhydrous. Stored at 130°C.
4. Methylene chloride, ACS, redistilled in glass.
5. Ethyl ether, AR, anhydrous.
6. Acetone, ACS, redistilled in glass.
7. Potassium Hydroxide, ACS, pellets.

Depending upon the amount of suspended material present, 1 or 2 liters of sample were placed in a glass separatory funnel fitted with a Teflon stopcock. The pH was adjusted to $\geq$ 11 with potassium hydroxide, and 100 mL of 15% methylene chloride in hexane was added. The funnel was shaken for at least 1 minute. The aqueous phase was transferred to a second separatory funnel and shaken with another 100 mL of the same solvent. The aqueous phase was transferred to a third separatory funnel and extracted with 100 mL of hexane. All three extracts were dried with a 2-inch anhydrous sodium sulfate column and drained into a 400 mL beaker. The aqueous phase was retained for acid extraction. The solvent was evaporated to ca. 5 mL by passing a gentle stream of filtered air over the beaker at room temperature, and the remaining solution was cleaned-up by column chromatography. The aqueous layer from the previous extraction was adjusted to pH less than 3 with 50% hydrochloric acid, and extracted

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with two 100 mL aliquots of chloroform. The chloroform extracts were combined and evaporated to dryness under a gentle stream of filtered air. The residue was redissolved in acetone and adjusted to an appropriate volume for injection into the gas chromatograph. Some acid extracts were methylated to verify compound identification and to facilitate analysis of more polar compounds.

B. Fish

Reagents

1. Dry Ice.

Apparatus

1. Laboratory blender and stainless steel blender jar.
2. Glass chromatography column, 350 mm by 20 mm id. with a 300 mL reservoir on top, a fritted glass disk at the bottom, and a Teflon stopcock to control the flow.

Fish tissue was blended with dry ice at high speed to produce a free-flowing powder. The dry ice was sublimed in a freezer for ca. 15 hours at -20°C. Ten grams of frozen fish were mixed with 60 grams of anhydrous sodium sulfate and allowed to stand for ca. 30 minutes with occasional stirring.

One-half inch of sodium sulfate was added to a chromatography column and the fish mixture was poured on top. The stopcock was opened and 200 mL of 10% ethyl ether in hexane was added. When the solvent had filled the column, the stopcock was closed slightly and the solvent eluted at ca. 5 mL/min.

Most of the solvent was evaporated and the extract quantitatively transferred to a tared beaker. The remaining solvent was evaporated and

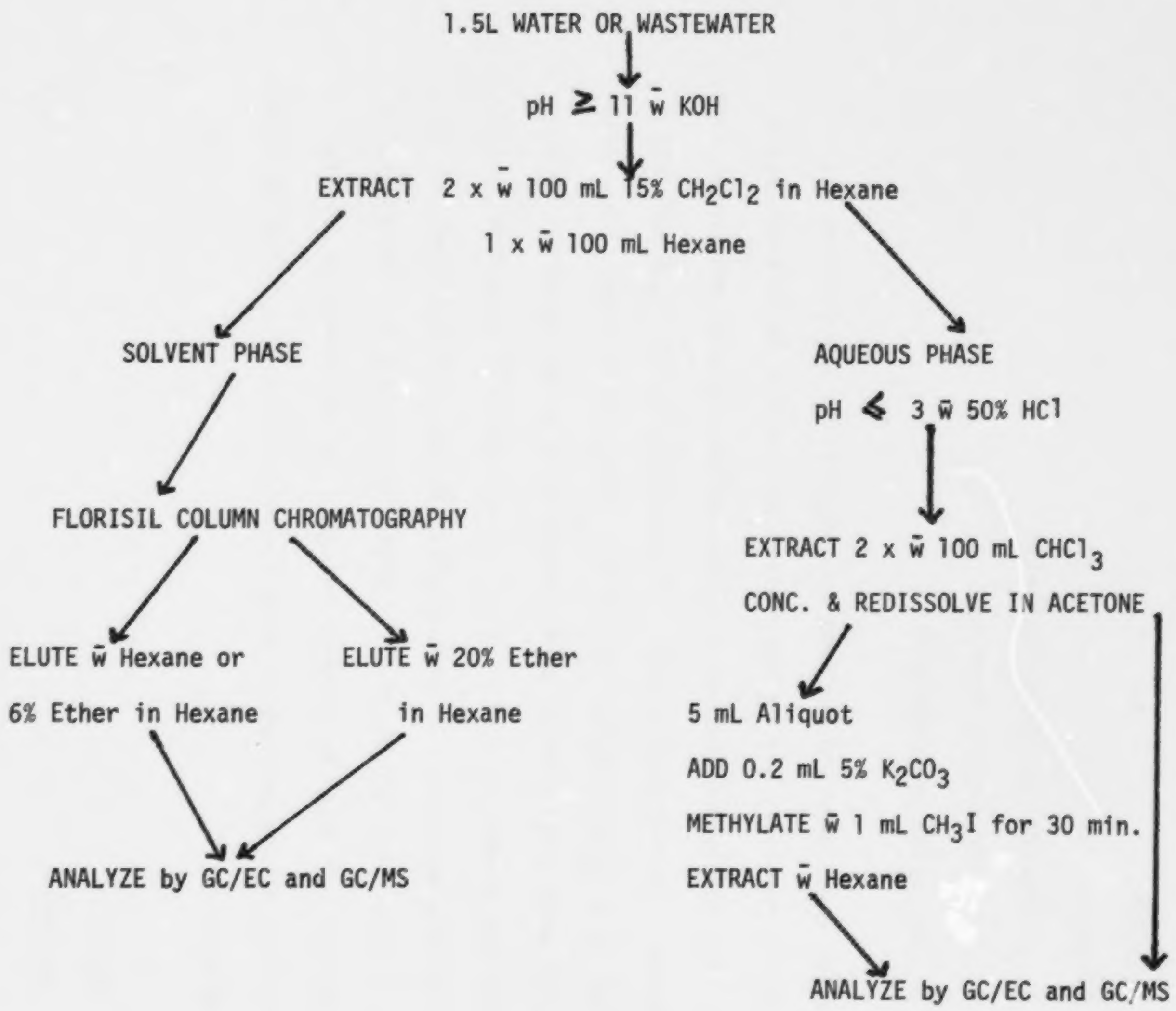

1.5L WATER OR WASTEWATER
pH ≥ 11 w̄ KOH
EXTRACT 2 x w̄ 100 mL 15% CH_2Cl_2 in Hexane
1 x w̄ 100 mL Hexane
SOLVENT PHASE
AQUEOUS PHASE
pH ≤ 3 w̄ 50% HCl
FLORISIL COLUMN CHROMATOGRAPHY
EXTRACT 2 x w̄ 100 mL $CHCl_3$
CONC. & REDISSOLVE IN ACETONE
ELUTE w̄ Hexane or
6% Ether in Hexane
ELUTE w̄ 20% Ether
in Hexane
5 mL Aliquot
ADD 0.2 mL 5% K_2CO_3
METHYLATE w̄ 1 mL CH_3I for 30 min.
EXTRACT w̄ Hexane
ANALYZE by GC/EC and GC/MS
ANALYZE by GC/EC and GC/MS

Figure 2. Water and Wastewater Extraction Procedure

the residue weighed to determine the fat content. The fat was redissolved in hexane and transferred to a Florisil column for clean-up by column chromatography.

C. Sediment

Apparatus

1. Extraction assembly, Soxhlet.
2. Paper extraction thimbles.
3. Hot plate or steam bath.

The water layer over the sediment was discarded. The sediment was allowed to partially air dry at ambient temperature in an evaporating dish. The sample was thoroughly mixed; stones, sticks, and leaves were discarded. The moisture content was determined by drying a separate portion in a tared container at 103°C. Twenty to 50 grams of air-dried sediment were mixed with an equal amount of granular anhydrous sodium sulfate and allowed to stand for ca. 30 minutes with occasional stirring. The sediment was placed in an extraction thimble and extracted for at least 8 hours with 300 mL of 1:1 acetone-hexane in a Soxhlet apparatus. The extract was dried by passage through a column of sodium sulfate. The solvent was evaporated to 10 mL and the extract cleaned-up by column chromatography.

D. Seston

Reagents

1. Hydrochloric acid, ACS, 1:1.
2. Chloroform, ACS, redistilled in glass.
3. Methylene chloride, ACS, redistilled in glass.
4. Sodium hydroxide, AR, 0.1 N.
5. Benzene, ACS, redistilled in glass.

The entire sample was acidified with 10 mL of 1:1 hydrochloric acid and diluted to 1 liter. The sample was extracted with two 100 mL aliquots of chloroform except methylene chloride was used for the last series of samples.

The resulting emulsion was mixed with two 100 mL aliquots of acetone and the extract filtered through Whatman No. 42 filter paper. The filtered acetone extract was combined with 500 mL of 0.1 N sodium hydroxide and extracted with 100 mL of hexane. This extract was retained for clean-up by column chromatography.

Twenty mL of 1:1 hydrochloric acid was added to the aqueous layer. The layer was then extracted with 100 mL of benzene and evaporated to an appropriate volume for injection into the gas chromatograph.

E. Suspended Solids

Ten to fifty mL of wastewater were vacuum filtered through Reeve Angel glass fiber filters (Grade 934 AH). The oven-drying techniques and calculations followed Standard Methods (84).

F. Centrifugation

Two 800 mL samples were centrifuged at 2000 RPM for 30 minutes to demonstrate PCB reduction by removal of solids. Both samples demonstrated *ca*. 50% reduction in PCB concentration.

CLEANUP COLUMN CHROMATOGRAPHY

Reagents

1. Florisil, pesticide reagent grade, 60-100 mesh, activated at 550°C for 15 hours stored at 160°C.

2. 94% hexane (Skelly solve B b.p. 60-68°C redistilled in glass)/ 6% ethyl ether, ACS

3. 80% hexane (skelly solve B b.p. 60-68°C redistilled in glass)/ 20% ethyl ether, ACS

Equipment

1. Glass chromatography column, 350 mm by 20 mm id. with a 300 mL reservoir on top, a fritted glass disk at the bottom, and a Teflon stopcock to control the flow.

The column was rinsed with acetone to dry the fritted disk and then rinsed with hexane. After the stopcock was closed, the column was filled to the base of the reservoir with hexane. One-half inch of granular anhydrous sodium sulfate was then added followed by 25 grams of florisil. Entrainment of air bubbles was avoided. One inch of sodium sulfate was added to the top. Next, the concentrated sample extract (ca. 5 mL) was added. The stopcock was opened and the column eluted at ca. 5 mL/min. The sample container was rinsed twice with a small amount of hexane and the rinses added to the column. When the solvent reached the top sulfate layer, 200 mL of hexane was added. The solvent was eluted again at a rate of ca. 5 mL/min. A solution of 94% hexane: 6% ether was later substituted for hexane in this method to elute more polar compounds in the first fraction. When the hexane (94% hexane/6% ethyl ether) portion reached the top sulfate layer, 200 mL of 80%

hexane/20% ethyl ether was added and the collection beaker changed. The column was then allowed to drain. When each aliquot of solvent had passed through the column, the solvent was reduced to a suitable volume by evaporation and analyzed by gas chromatography/electron capture (GC/EC) and gas chromatography/mass spectrometry (GC/MS).

METHYLATION

Reagents

1. Acetone, ACS, redistilled in glass.
2. Potassium carbonate, AR.
3. Methyl iodide, Aldrich, 99%.

The acid extract was dissolved in 5 mL of acetone in a 50 mL screw-top centrifuge tube, and 0.2 mL of 5% potassium carbonate and 0.5 mL of methyl iodide were added. The mixture was allowed to react at room temperature for *ca*. 30 minutes. The acetone and methyl iodide were evaporated to *ca*. 0.5 mL with a gentle stream of clean, dry air. One gram of anhydrous sodium sulfate was added to remove water. The solution containing the methylated derivatives was quantitatively transferred to a graduated centrifuge tube and diluted with hexane to an appropriate volume for injection into the gas chromatograph.

ANALYSIS BY GAS CHROMATOGRAPHY

Equipment

1. Gas chromatograph (Perkin Elmer model 3920 or Hewlett Packard model 402) with electron capture dector (63_{Ni}).

Conditions:

Injectors: 250°C.

Columns: 200°C.

Detectors: 230° to 300°C.

2. GLC columns, glass, 1.8 m by 4 mm i.d. Packings:
   6% SP-2401/4% SE 30 on Supelcoport 100/120 mesh.
   10% SP-1000/1% Phosphoric acid on Supelcoport 80/100 mesh.

3. Strip chart (Perkin Elmer model 690) or integrating recorder (Hewlett Packard model 3380A)

4. Ten uL syringe.

Twenty-five to 50 mg of an Aroclor PCB mixture was dissolved in hexane and diluted in a volumetric flask to give a concentration of 2.0 ug/mL. Four to 8 uL of standard was injected into the gas chromatograph to determine the linear range of the detector. Samples were diluted as necessary to ensure that they were in the same order of magnitude as the standard (s).

Four to 8 uL of the sample was injected and PCB or chloro-organic compounds were identified by retention times and/or fingerprint patterns. Peak heights were measured and matched to the standards. The concentration of each compound was calculated using the peak height method (strip charts) or peak area method (integrating recorder).

Extraction and analysis methods were adapted from Hesselberg and Johnson (85), Thompson (86) and the U.S. EPA (87).

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GC/MS System

The identification and confirmation of compounds in this project were accomplished using a Finnigan gas chromatograph (model 9500)/mass spectrometer (model 3100D) with an on-line computer data system (model 6000) and a Zeta X-Y plotter. Electron impact mass spectra ranging from m/z 35-500 were acquired at an emission current of 0.35 milliamps, electron energy of 70 eV., amplification of 10^{-7} amp./Volt, and electron multiplier setting of 2.10 kV. The GC/MS was calibrated with perfluorotertiarybutylamine (FC-43) whenever ions of known samples of aldrin, chloro-phenols, chloroanisoles, or polychlorinated biphenyls (PCBs) were not well resolved or exhibited shifted m/z ratios as evidenced by abnormal ion abundances for the number of chlorines present in the standards. The resolution of FC-43 was adjusted to agree with specifications given by Carter (74). Known compounds were analyzed daily as part of a quality assurance program to document column efficiency and overall GC/MS system performance.

Experimental Approach

Several months were spent exploring different GC/MS conditions and evaluating column packings that were best suited to suspected compounds in the sample fractions. A retention index relative to aldrin was employed to help identify and locate compounds detected by a gas chromatograph with an EC detector (GC/EC). (See Appendix C for a relative retention index of acid fraction compounds that were chromatographed either directly or as methylated derivatives on Ultra-Bond 20M).

GC/MS Column Selection

Glass columns were packed with 3% SE-30 on 80/100 mesh Gas Chrom 9-3% SP-2100 on Supelcoport 100/120 mesh or physically bonded Ultra-Bond 20M on 100/120 mesh Chromosorb W (loading ca. 0.2% Carbowax 20M). Column lengths were either 1.8 or 3 m x 2 mm i.d. The SE-30 and SP-2100 columns were temperature programmed from 100 to 220°C at 4°/min when neutral extracts (hexane, 94% hexane/6% ethyl ether and 80% hexane/20% ethyl ether) were analyzed. The Ultra-Bond 20M columns were programmed either from 90 to 210°C (1.8 m column) or 110 to 250°C (3 m column) at 4°/min. to analyze both methylated and nonmethylated acid fractions as well as for general purpose analyses. All column packings were obtained from commercial sources. The injector and glass jet separator heaters were set at ca. 250°C. Helium carrier gas flow varied between 20 to 30 mL/min based on the optimum separator efficiency with a vacuum not exceeding 6×10^{-6} Torr.

GC/MS Operation

The GC/MS was programmed to integrate spectra at the following times: 4 millisec (ms) from m/z 35 to 150, 8 ms from m/z 151 to 300, and 12 ms from m/z 301 to 500, resulting in 4 second scans. Occasionally integration times were changed to 4 ms from m/z 35 to 150, 9 ms from m/z 151 to 300 and 12 ms from m/z 301 to 350 or 400, resulting in 3-second scans. The sample run time ranged from 10 to 35 minutes depending on the number of peaks detected by GC/EC. The GC/MS data system displayed a Total Ion Chromatogram (TIC) that resembled a gas chromatogram.

The ions of compounds eluting at various retention times were detected as peaks on the TIC. These peaks were investigated with the data system to search the entire mass spectra for a specific ion or ion cluster of each compound. The Limited Mass Reconstructed Gas Chromatogram (LMRGC) and/or TIC were used to choose an appropriate background spectrum and to determine isomers, closely related compounds, and compounds with similar (interfering) retention times. Compounds in sample extracts were identified by various means as described in Appendix A. One way was to compare the retention time and mass spectrum of a suspected constituent with those of a standard of that compound. Another way was to compare the full or partial mass spectrum (8 most abundant ions) of a constituent with published spectra, e.g. The Eight Peak Index of Mass Spectra (78). For several unknown compounds, mass spectra were compared with the Finnigan GC/MS data system library of about 1,000 abbreviated spectra of pesticides, drugs, and industrial chemicals. A mass spectrum remaining unidentified after these processes was interpreted by the abundance or lack of an apparent molecular ion, known fragmentation patterns, and isotopic abundances. For instance, if the compound was chlorinated (e.g. trichlorophenol Appendix D-19), the number of chlorines on the molecule could be noted according to isotopic abundances. An abundant molecular ion usually implies an aromatic compound (e.g. phenol). A small or absent molecular ion implies at least some substitution (e.g. ethyl phenol Appendix E-14). A compound with a strong molecular ion showing a loss of 1 m/z suggests a labile hydrogen as seen in the spectra of vanillin (Appendix D-23) and syringaldehyde (Appendix D-22).

GC/MS/ INTERPRETIVE ANALYSIS

The sample selected for a detailed interpretive analysis here was an acid extract of the Bergstrom Paper Company final effluent, which is discharged into Little Lake Butte des Morts. The sample was extracted according to the procedure outlined on page 21. This extract was first analyzed by GC/EC and then GC/MS to determine the presence of methylated compounds (e.g. chloro-anisoles, chloro-veratroles, and resin acid esters) prior to any further sample treatment. A TIC for this sample is shown in Figure 3. No methylated compounds were found in this extract.

The extract contained small quantities of chloro-phenols and chloro-guaiacols, along with dehydroabietic acid. However, in order to facilitate improved gas chromatographic analysis and to detect more polar compounds that do not elute well off a GC column, methylated derivaties were prepared according to the procedure outlined on page 25. The TIC of this extract after methylation is shown in Figure 4. Figure 5 shows an expanded amplitude scale with peak identification. Upon methylation, chloro-phenols are converted to chloro-anisoles, chloro-guaiacols become chloro-veratroles, and dehydroabietic acid becomes methyl dehydroabietate.

The mass spectra of the various compounds identified in this sample were compared with mass spectra obtained by injecting pure compounds into the GC/MS system under identical operating conditions as well as mass spectra in the literature and data system library. Mass spectra of compounds found in this sample compared with standard spectra are included in Appendix D in alphabetical order. Mass spectra of compounds compared with published mass spectra are presented in Appendix E. Mass spectra of compounds unidentified or tentatively identified are presented in Appendix F.

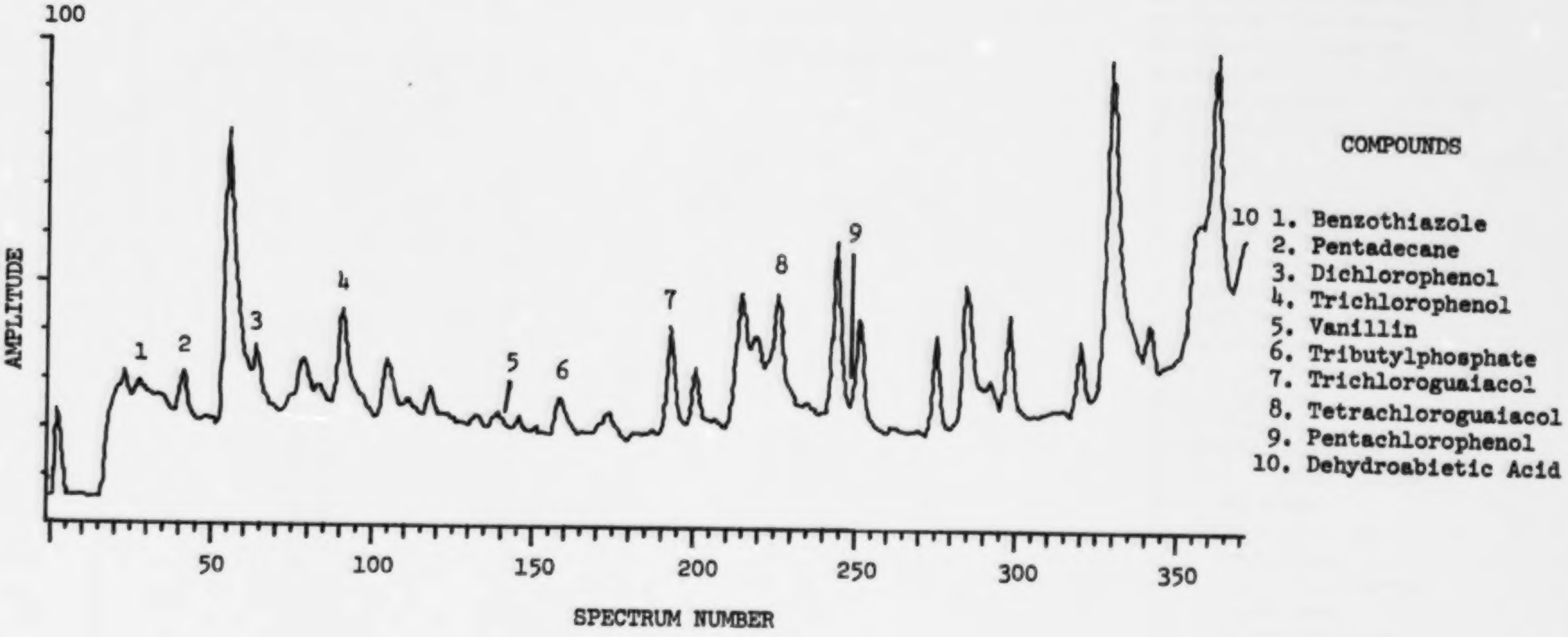


Figure 3. Total Ion Chromatogram: Acid Extract Of A Paper Mill Effluent (Nonmethylated)

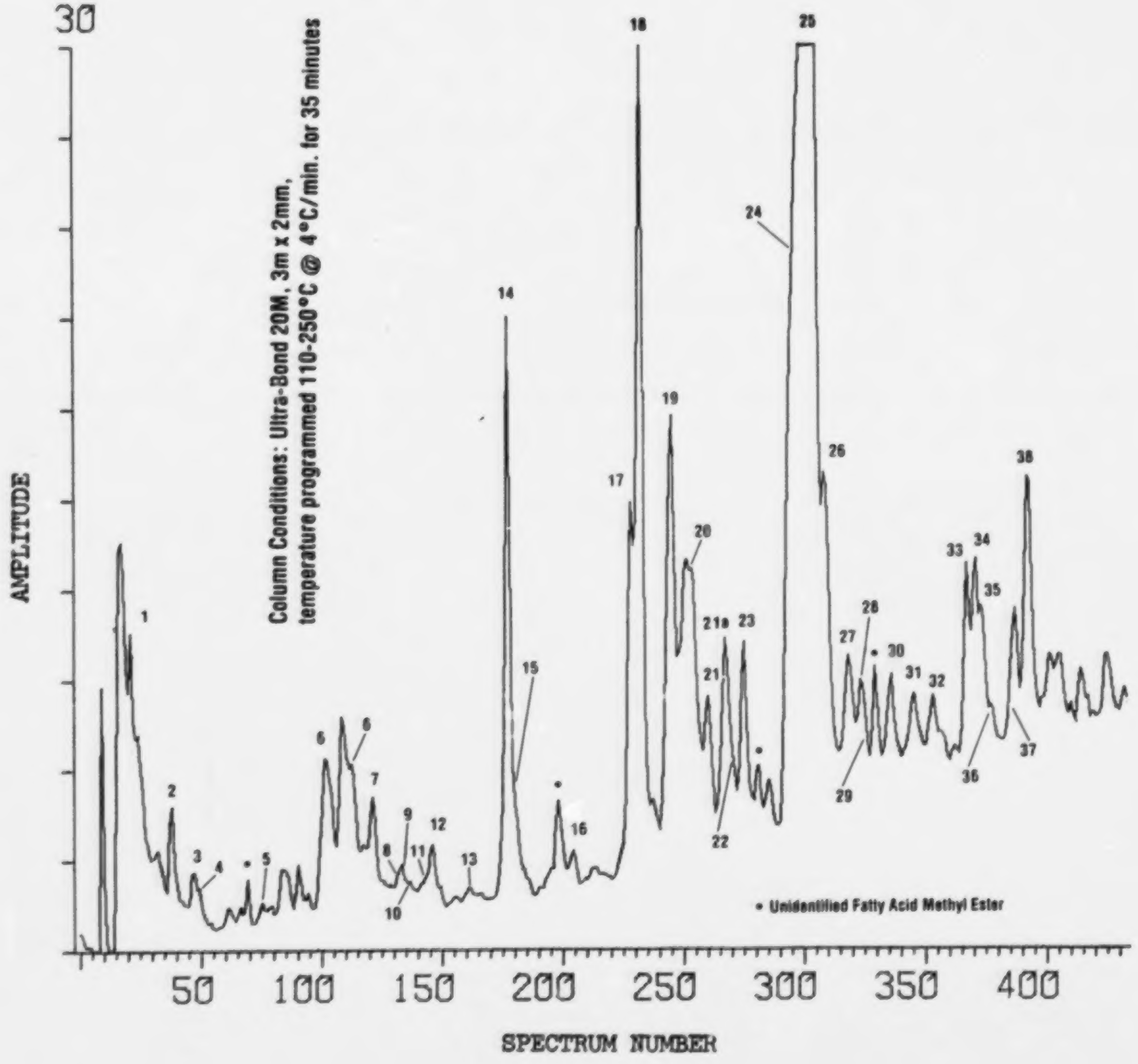


Figure 4. Total Ion Chromatogram: Methylated Acid Extract Of A Paper Mill Effluent

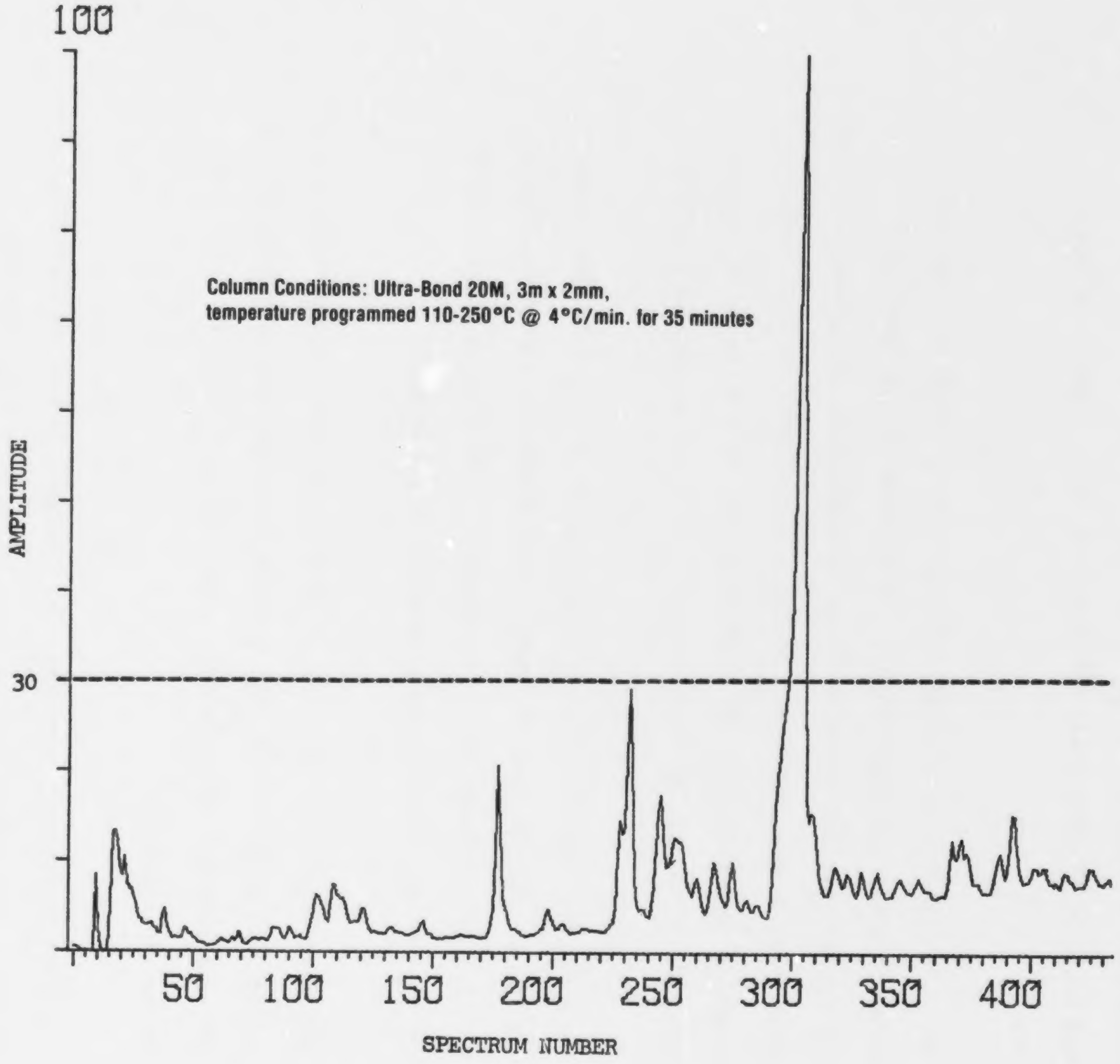
COMPOUNDS

1. Chloroanisole
2. 2, 4, 6 - Trichloroanisole
3. Dichloroanisole
4. Benzothiazole
5. Tetrachloroanisole
6. Nonyl anisole
7. Pentachloroanisole
8. Tetrachloroveratrole
9. Methyl thiobenzothiazole
10. Trichloroveratrole
11. Trichloro-trimethoxybenzene
12. Tributyl phosphate
13. Methoxybenzothiazole
14. Methyl palmitate
15. Aldrin — External standard
16. Methyl heptadecanoate
17. Methyl oleate
18. Methyl stearate
19. Methyl 8, 15 - isopimardien-18-oate
20. Methyl pimarate
21. Methyl sandaracopimarate

21 a. Bisphenol a dimethyl ether

22. Unidentified R A M E* (MW 318)
23. Unidentified R A M E (MW 316)
24. Unidentified R A M E (MW 328)
25. Methyl dehydroabietate
26. Methyl 6, 8, 11, 13-abietatetraen-18-oate
27. Unidentified R A M E (MW 328)
28. Dichloro-bisphenol a dimethyl ether
29. Chloro-bisphenol a dimethyl ether
30. Chloro R A M E (MW 362)
31. Chloro-methyl dehydroabietate (A)
32. Chloro-methyl dehydroabietate (B)
33. Tetrachloro-bisphenol a dimethyl ether
34. Dioctyl phthalate
35. Trichloro-bisphenol a dimethyl ether
36. Dichloro-bisphenol a dimethyl ether
37. Dichloro-methyl dehydroabietate (MW 382)
38. Methyl oxo-dehydroabietate (MW 328)

*R A M E = Resin Acid Methyl Ester



Column Conditions: Ultra-Bond 20M, 3m x 2mm,
temperature programmed 110-250°C @ 4°C/min. for 35 minutes

Figure 5. Total Ion Chromatogram: Methylated Acid Extract of a Paper Mill Effluent

Mass spectra and LMRGCs of some of the compounds found in this methylated extract are presented here as Figures 6 through 19. Mass spectra indicate how molecules fragment when ionized by electrons. The LMRGC is a data system function that helps identify a specific compound by searching for one or more distinguishing ions in the mass spectra of a sample. These ions could be the base peak, molecular ion and/or isotopic molecular ions.

Peak 2 in Figure 5 is 2,4,6-trichloroanisole. Five other trichloroanisole isomers are also possible. This isomer is the least polar trichloroanisole and elutes early on the Ultra-Bond 20M column. Trichloroanisole has a molecular weight of 210 (^{35}Cl isotope) and with isotopic molecular ions unique for three chlorine ions on a molecule ($M^{+\cdot}$ = 100%, $M^{+\cdot} + 2$ = 98%, $M^{+\cdot} + 4$ = 31%, $M^{+\cdot} + 6$ = 3%) as seen in Figure 6.

The LMRGC for 2,4,6-trichloroanisole is given in Figure 7. The isotope m/z 210 was used to draw the LMRGC. Scan Number 37 (peak 2) in Figure 5 is 2,4,6-trichloroanisole. The peaks at later elution times contain the ion m/z 210, but they have higher molecular weights.

Peak 3 in Figure 5 is an isomer of dichloroanisole. Dichloroanisole has a molecular weight of 176 with isotopic molecular ions equivalent to two chlorine ions on a molecule ($M^{+\cdot}$ = 100%, $M^{+\cdot} + 2$ = 65%, $M^{+\cdot} + 4$ = 11%) as seen in Figure 8.

The LMRGC in Figure 9 represents the isotope (m/z 176) of dichloroanisole. Scan Number 47 (peak 3) on Figure 5 is dichloroanisole. Several other compounds also have m/z 176 in them, as noted by the later eluting peaks, but they have much larger molecular weights.

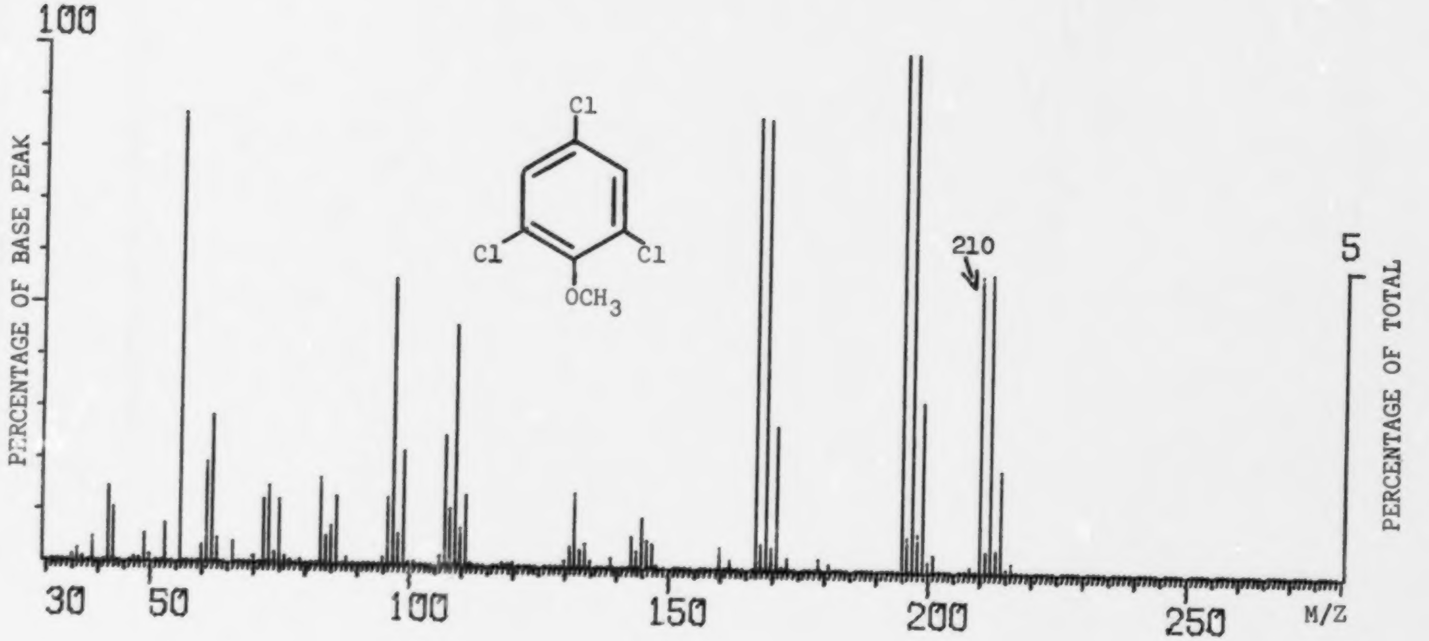


Figure 6. 2,4,6, Trichloroanisole (Mass Spectrum of Peak 2 From Fig. 4)

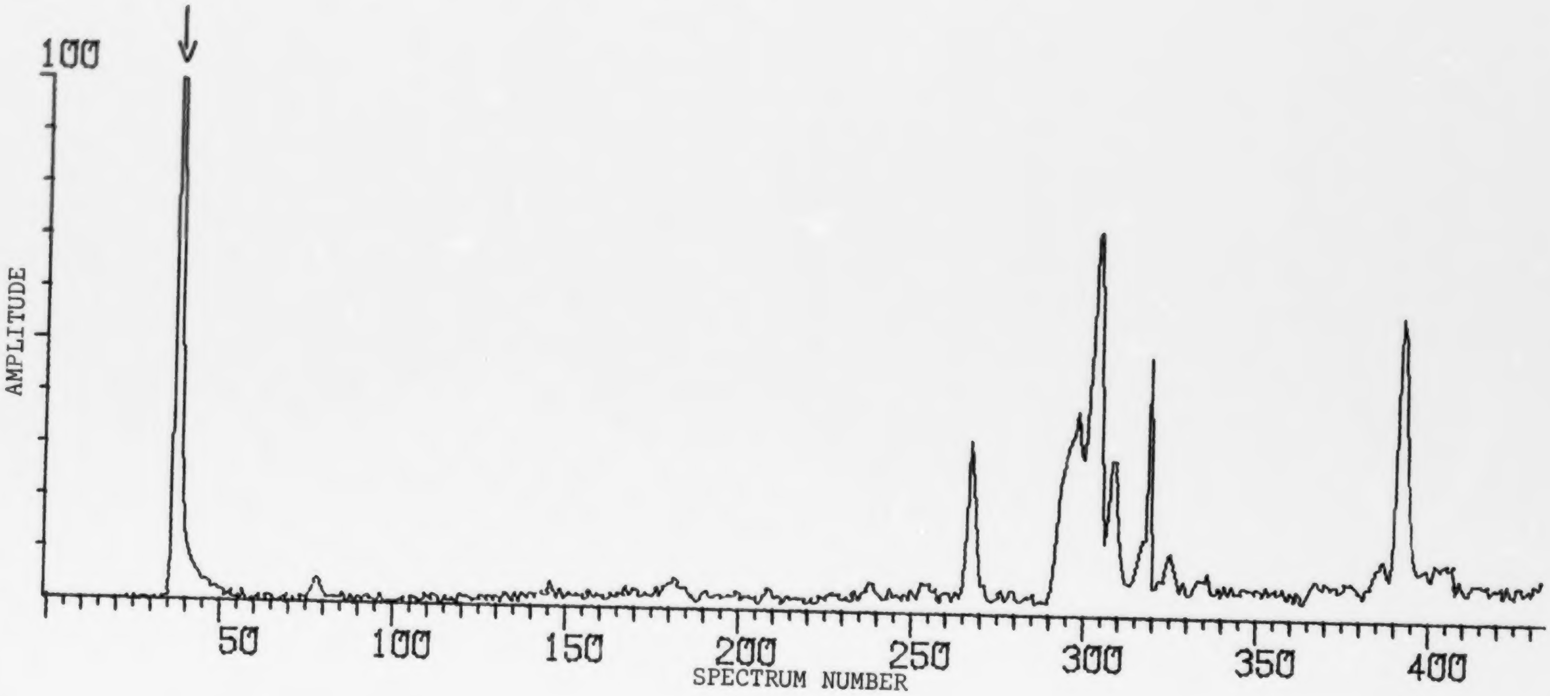


Figure 7. Limited Mass Reconstructed Gas Chromatogram (LMRGC) of 2,4,6, Trichloroanisole
M/Z 210

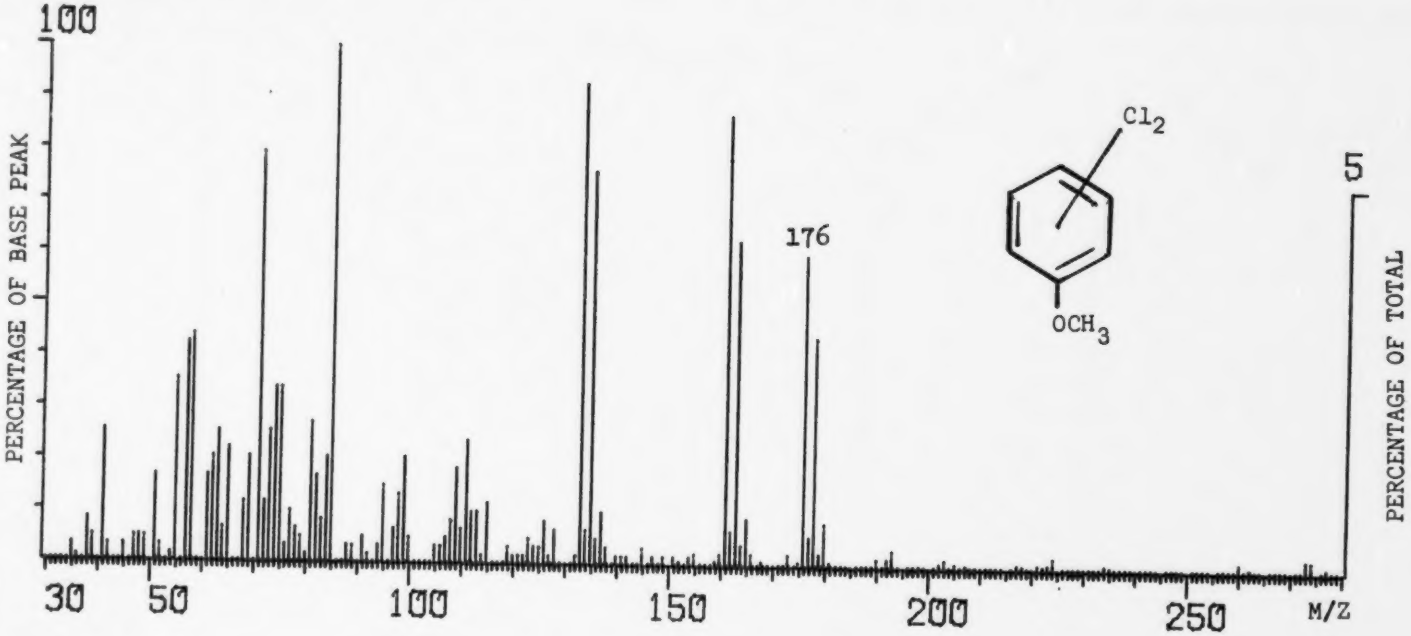


Figure 8. Dichloroanisole (Mass Spectrum of Peak 3 from Fig. 4)

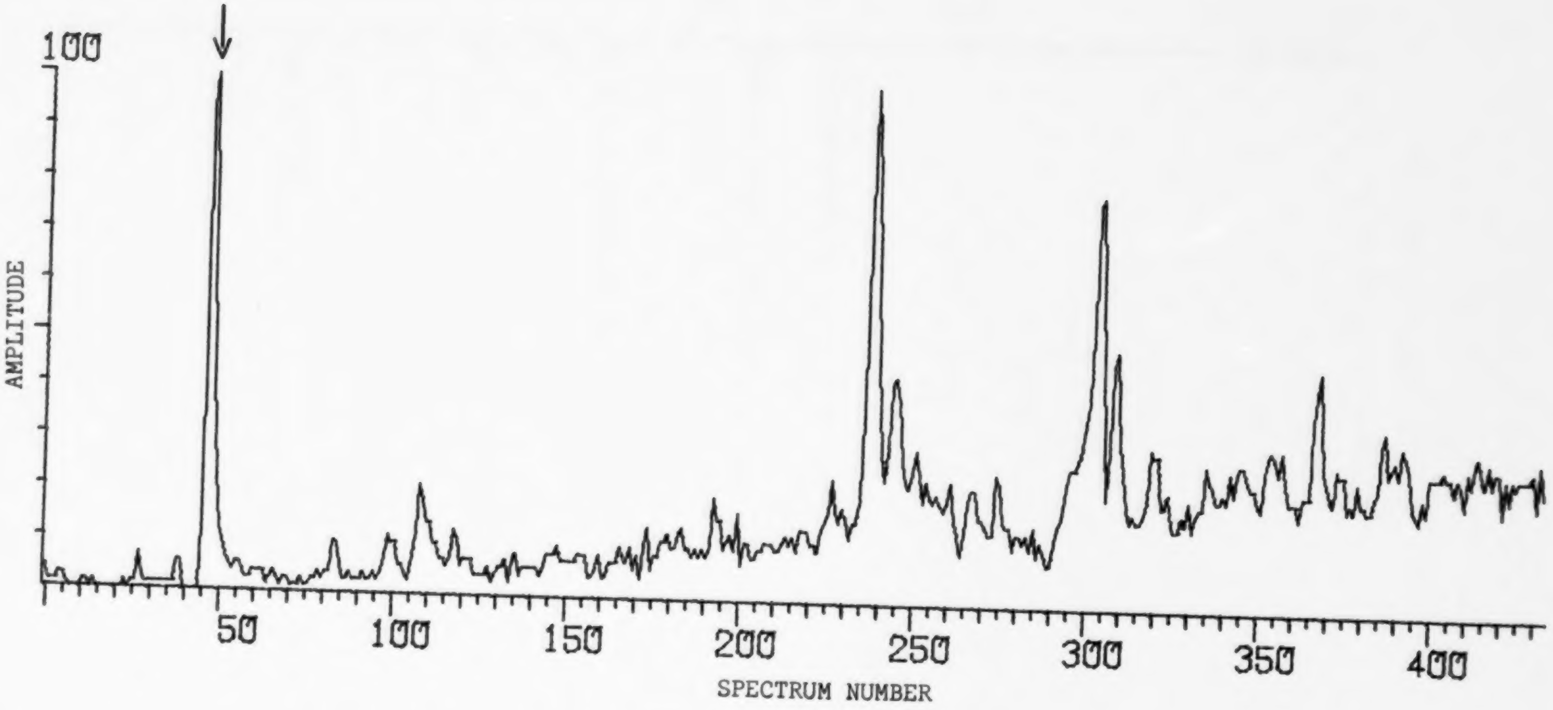


Figure 9. LMRGC of Dichloroanisole M/Z 176

Benzothiazole is peak 1 in Figure 3 and peak 4 in Figure 5. The benzothiazole molecule was not methylated under the conditions given. The mass spectrum (Figure 10) for benzothiazole indicates an odd-numbered molecular ion (135). This suggests a compound with an odd number of nitrogen atoms. The mass spectrum does not show a methyl loss (M - 15)+.

The LMRGC for the molecular ion (m/z 135) and the second most abundant ion (m/z 108) of benzothiazole is found in Figure 11. Scan Number 50 in Figure 11 is benzothiazole. The later eluting peaks all have higher molecular weights.

The mass spectrum of pentachloroanisole is shown in Figure 12. The spectrum shows the definite isotopic molecular ions for five chlorine atoms on a molecule ($M^{+\cdot}$ = 61%, $M^{+\cdot}$ + 2 = 100%, $M^{+\cdot}$ + 4 = 65%, $M^{+\cdot}$ + 6 = 21%, $M^{+\cdot}$ + 8 = 37%). Peak Number 7 in Figure 5 is pentachloroanisole.

The LMRGC for pentachloroanisole is provided in Figure 13. The two most abundant isotopic molecular ions for pentachloroanisole, m/z 280 and 282, were used.

Peak 8 in Figure 5 is tetrachloroveratrole. Its mass spectrum is found in Figure 14. The spectrum has the typical ion cluster for four chlorine ions on a molecule ($M^{+\cdot}$ = 77%, $M^{+\cdot}$ + 2 = 100%, $M^{+\cdot}$ + 4 = 49%, $M^{+\cdot}$ + 6 = 10%) at m/z 274.

The isotopic molecular ion m/z 274 of tetrachloroveratrole indicates that scan Number 132 in Figures 5 and 15 is its retention time. The later eluting peaks have higher molecular weights.

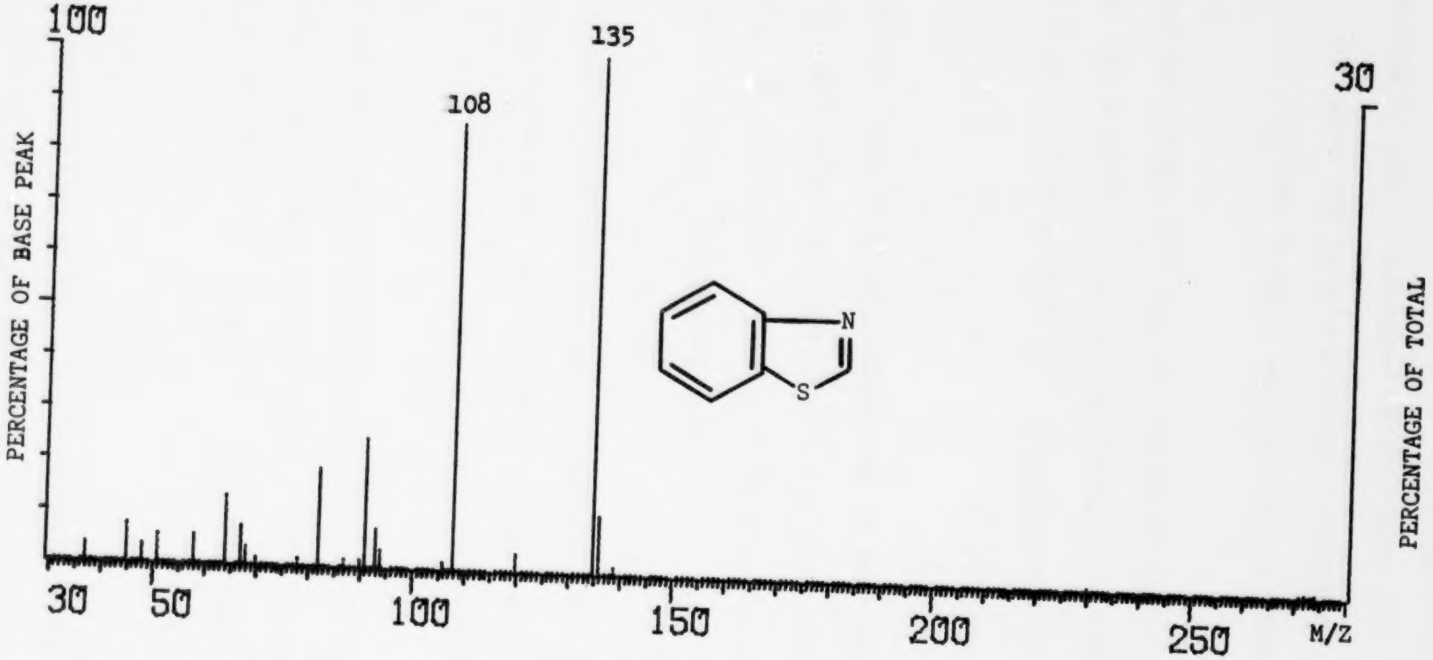


Figure 10. Benzothiazole (Mass Spectrum of Peak 4 from Fig. 4)

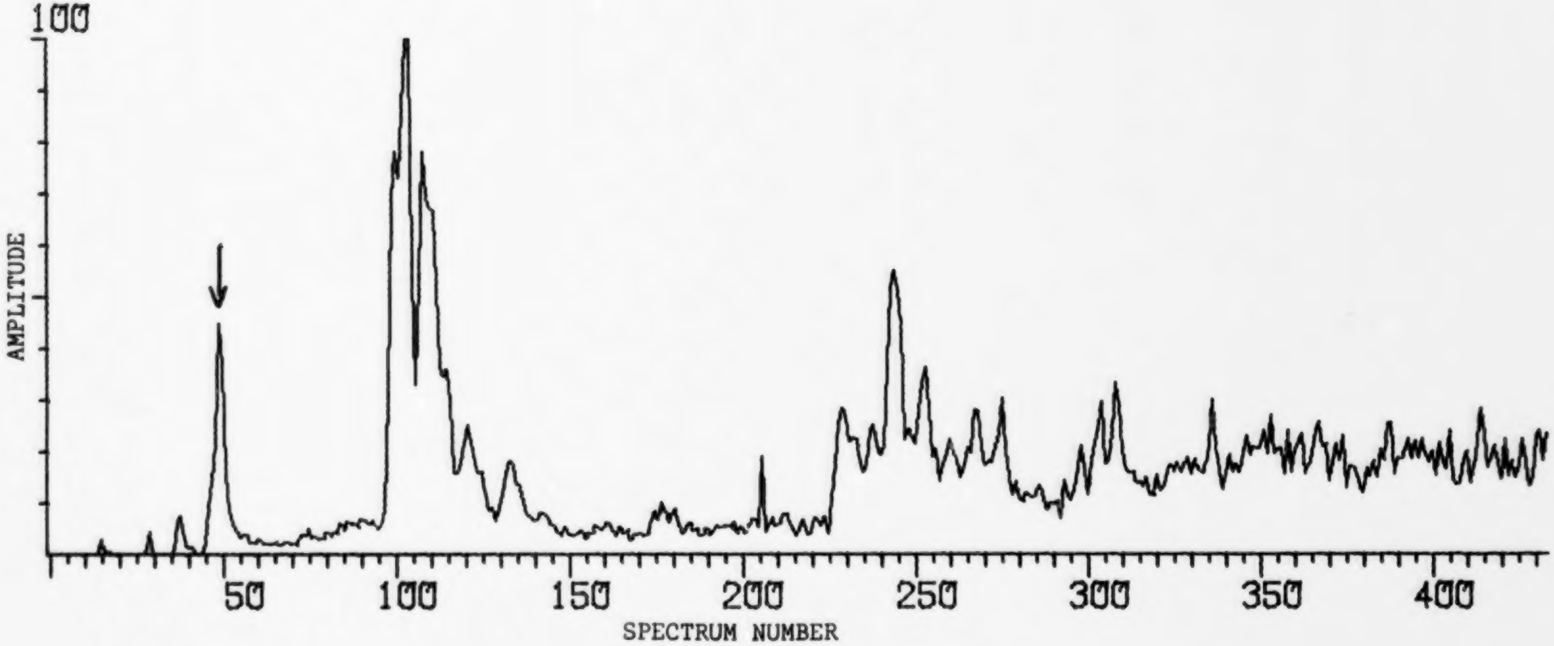


Figure 11. LMRGC of Benzothiazole M/Z 108 and 135

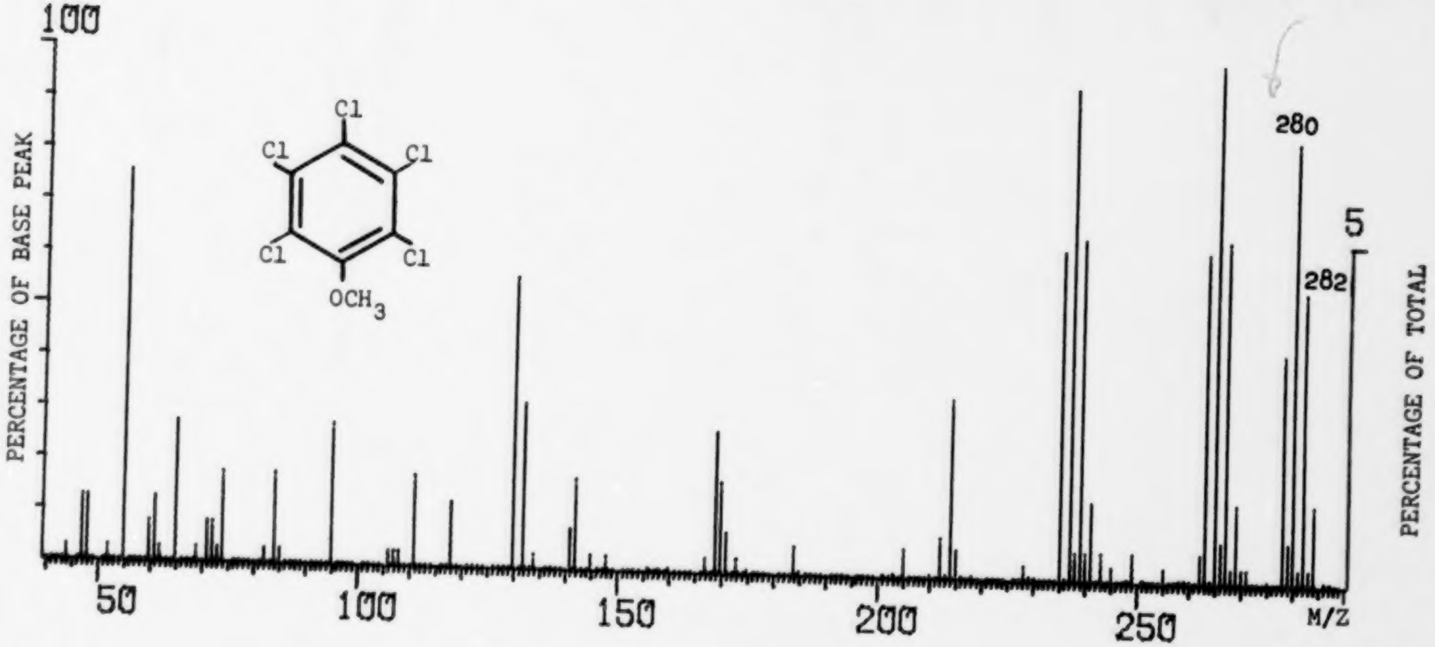


Figure 12. Pentachloroanisole (Mass Spectrum of Peak 7 from Fig. 4)

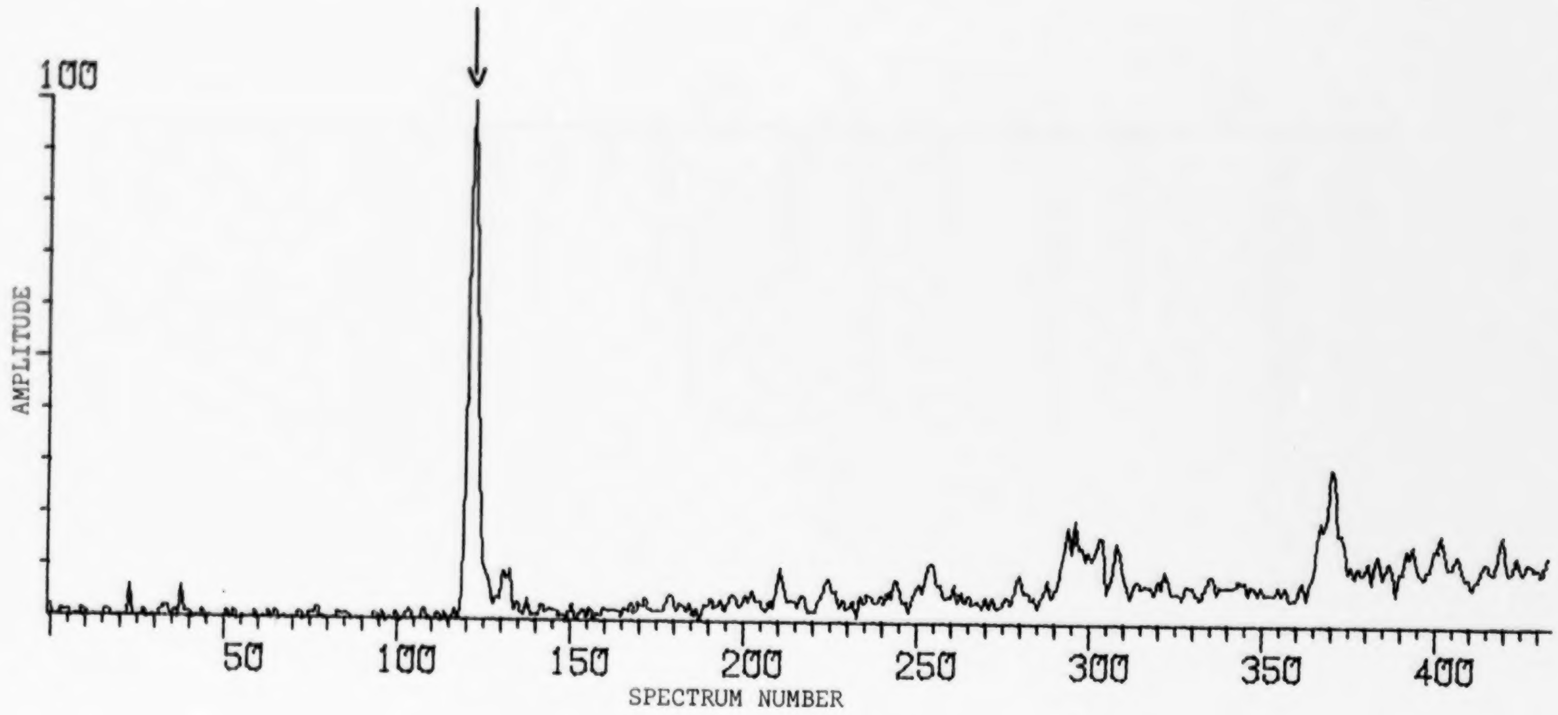


Figure 13. LMRGC of Pentachloroanisole M/Z 280 and 282

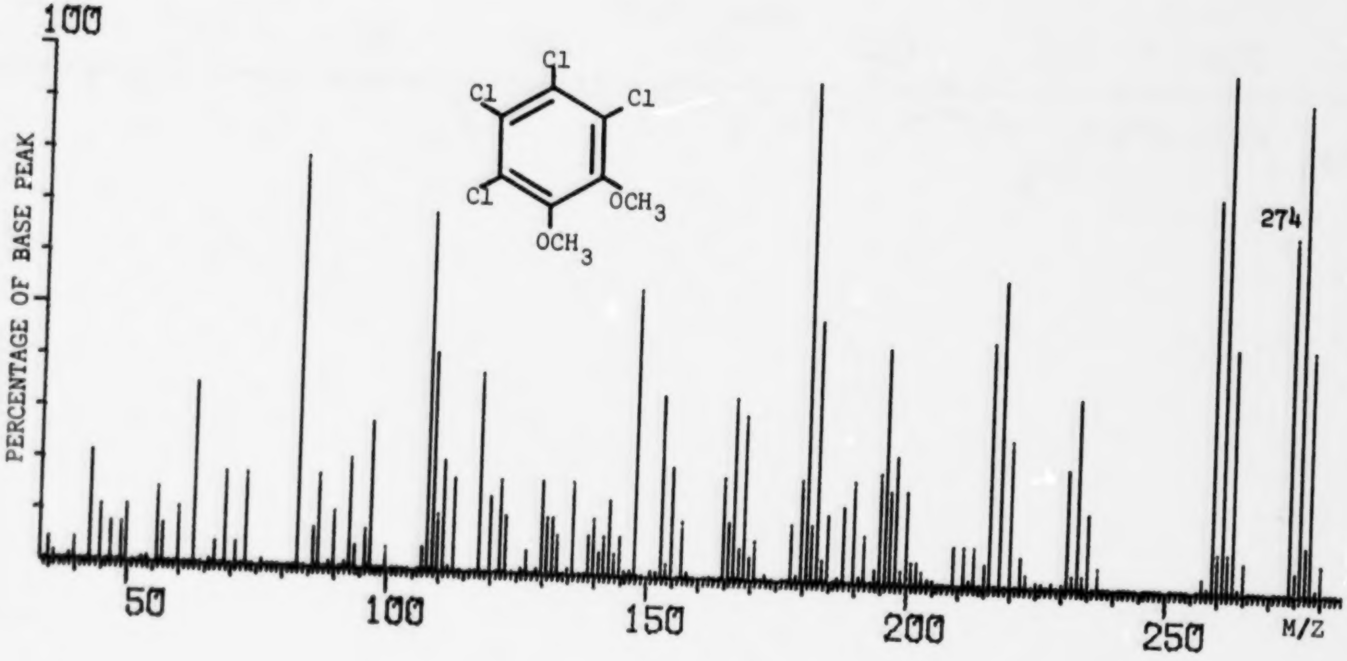


Figure 14. Tetrachloroveratrole (Mass Spectrum of Peak 8 from Fig. 4)

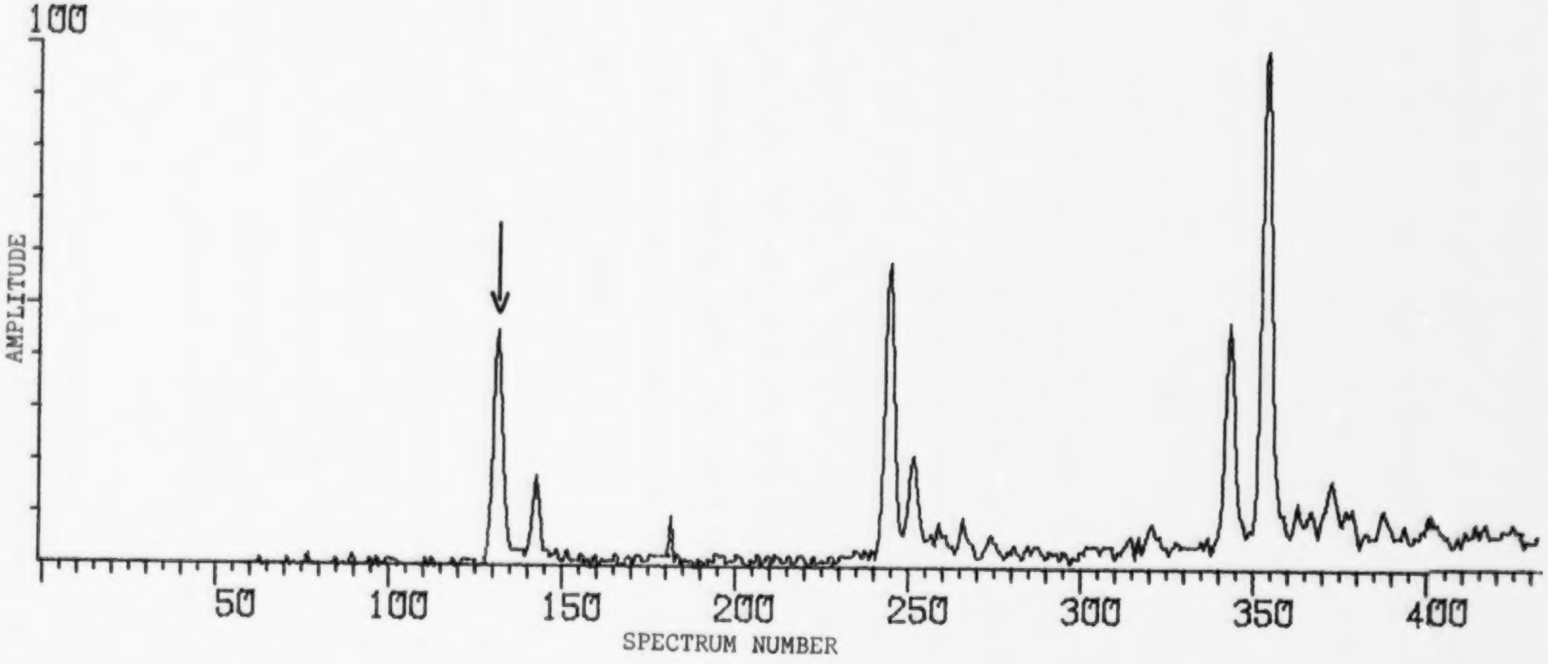


Figure 15. LMRGC of Tetrachloroveratrole M/Z 274

Peak Number 25 in Figure 5 is methyl dehydroabietate. Its mass spectrum is illustrated in Figure 16. The spectrum shows the molecular ion, $M^{+\cdot}$, at m/z 314. Principal fragment ions are $(M - 15)^+$ at m/z 299 and the most abundant ion or base peak $(M - 75)^+$ at m/z 239 corresponding to losses of methyl (CH_3) and (CH_3 + $HCOOCH_3$), respectively. The LMRGC of its molecular ion m/z 314, in Figure 17, shows only one peak at scan Number 299 and corresponds to peak 25 in Figure 5.

The mass spectrum of one of two isomers of methyl chlorodehydroabietate can be seen in Figure 18. The spectrum is very similar to that of methyl dehydroabietate except for an upward shift of m/z 34 (314 + 34 = 348). The isotopic molecular ions m/z 348 (100%) and 350 (33%) are consistent for one chlorine atom on a molecule. Principal fragment ions are $(M - 15)^+$ at m/z 333 and the base peak $(M - 75)^+$ at m/z 273 corresponding to the same losses described for methyl dehydroabietate. The exact positions of the chlorine atom in the molecule for the two isomers were not easily determined. Since both spectra exhibited the same fragmentation as methyl dehydroabietate without any discernible loss of an HCl molecule, Trost (80) proposed that the chlorine atom was on the aromatic ring. These probable positions marked X on Figure 18 were those verified by ^{13}C and ^{1}H NMR in Thakore and Oehlschlager (63). The mass spectra and relative retention times of these isomers were consistent with synthesized standards furnished by Leach and Thakore (BC Research, Vancouver, British Columbia) and previously published data (26, 63).

The LMRGC for methyl chlorodehydroabietate, using the most abundant ion (m/z 273) in the spectrum, is found in Figure 19. The two peaks at scan Numbers 243 and 253 both have the same molecular weight but elute at different retention times.

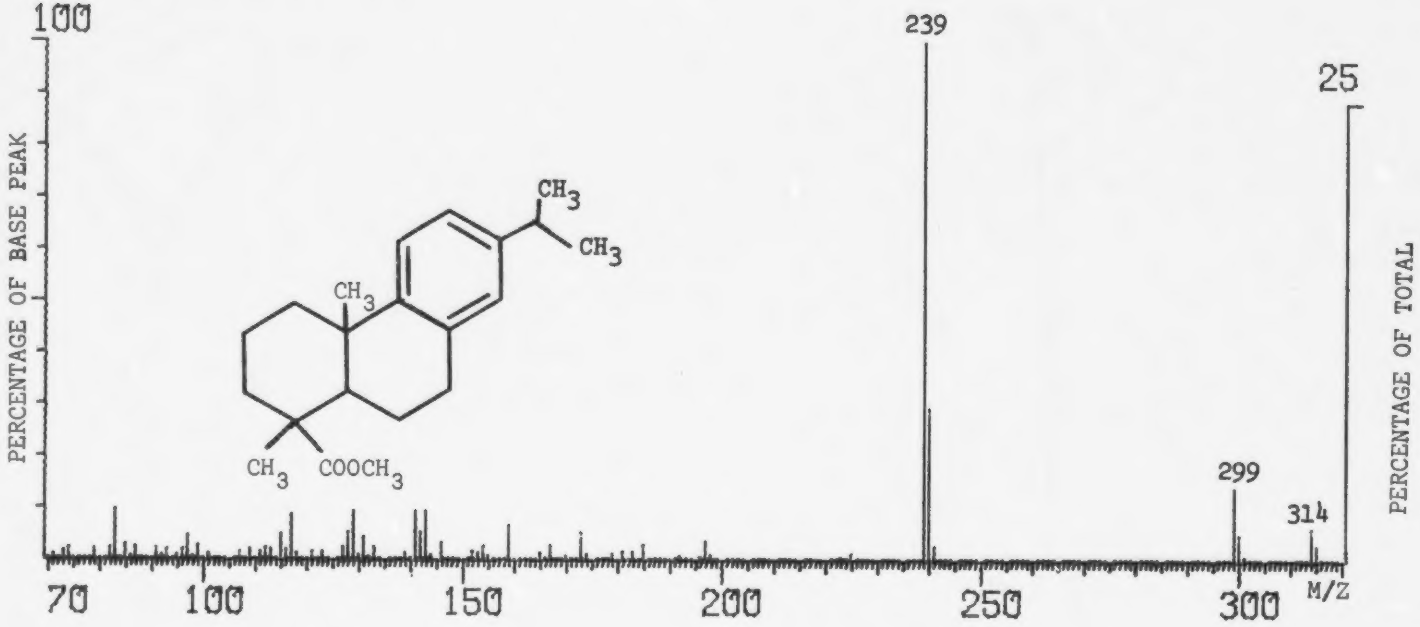


Figure 16. Methyl Dehydroabietate (Mass Spectrum of Peak 25 from Fig. 4)

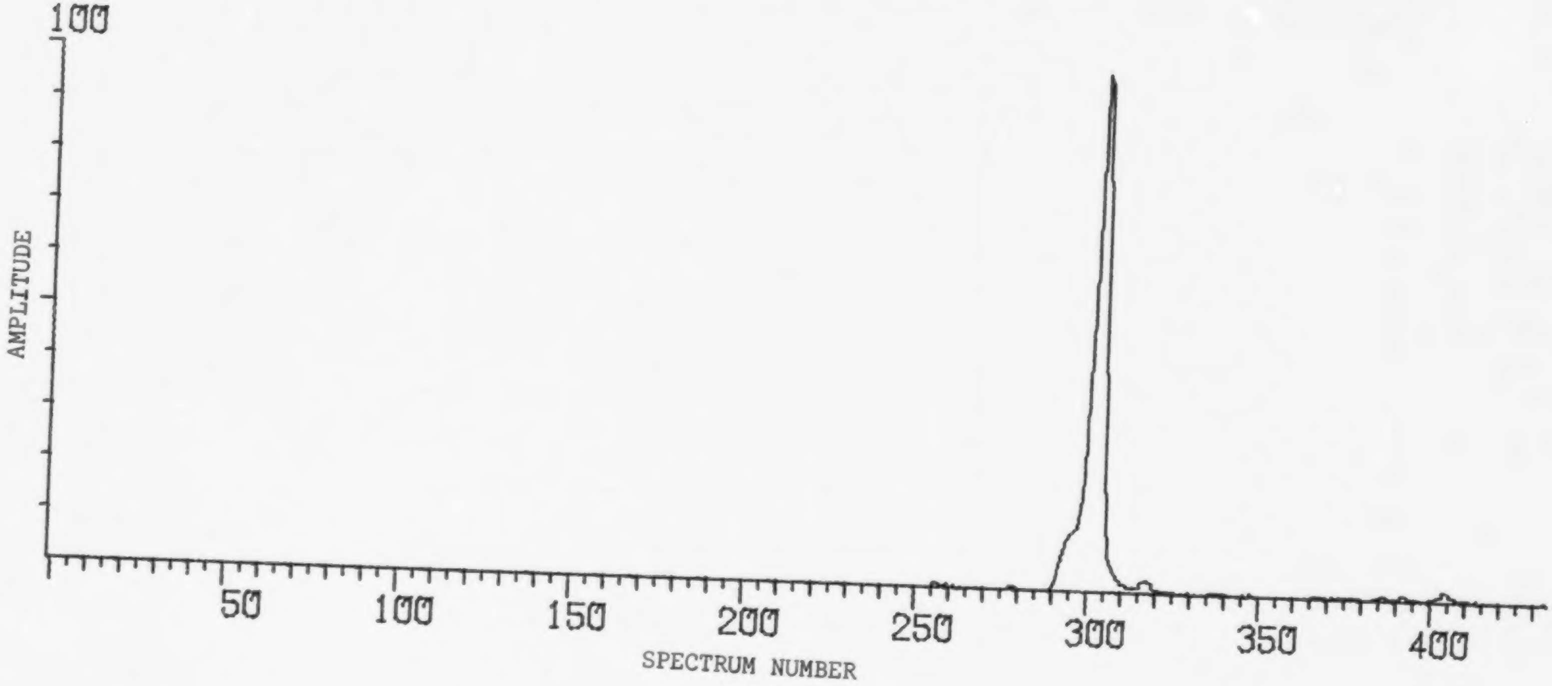


Figure 17. LMRGC of Methyl Dehydroabietate M/Z 314

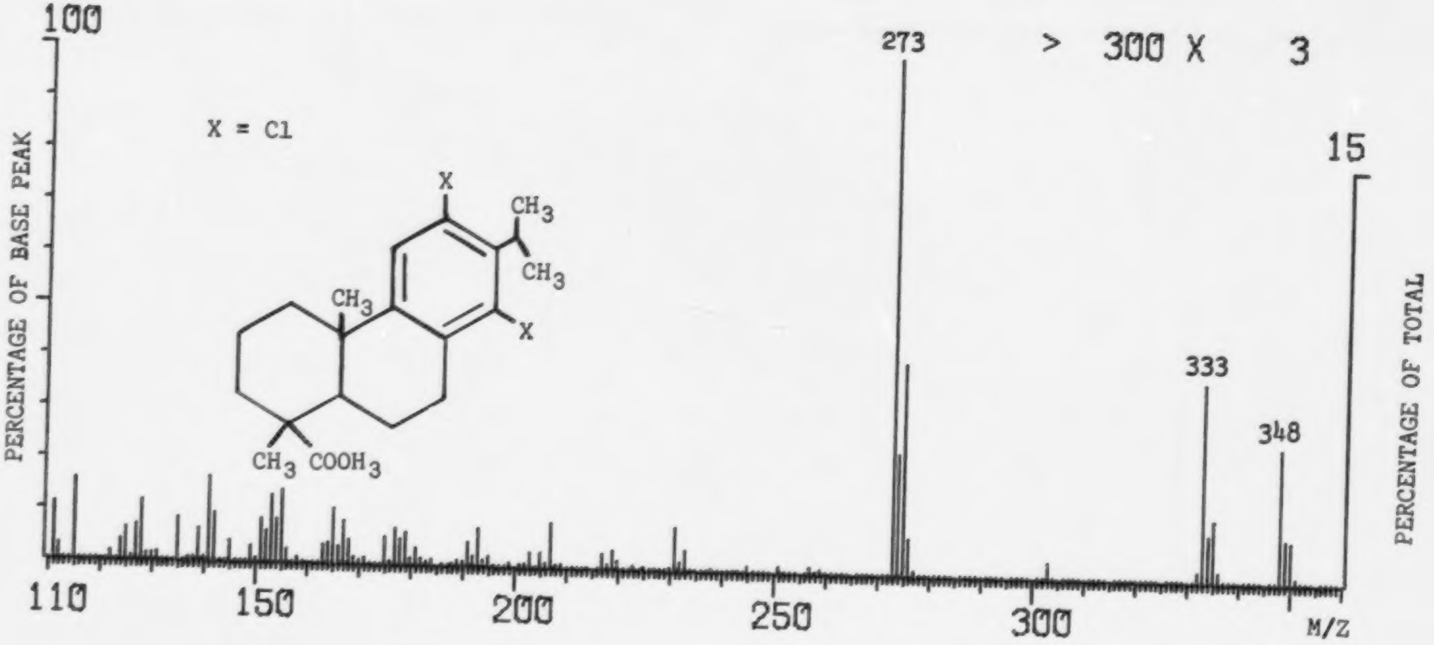


Figure 18. Methyl Chlorodehydroabietate (Mass Spectrum of Peak 32 from Fig. 4)

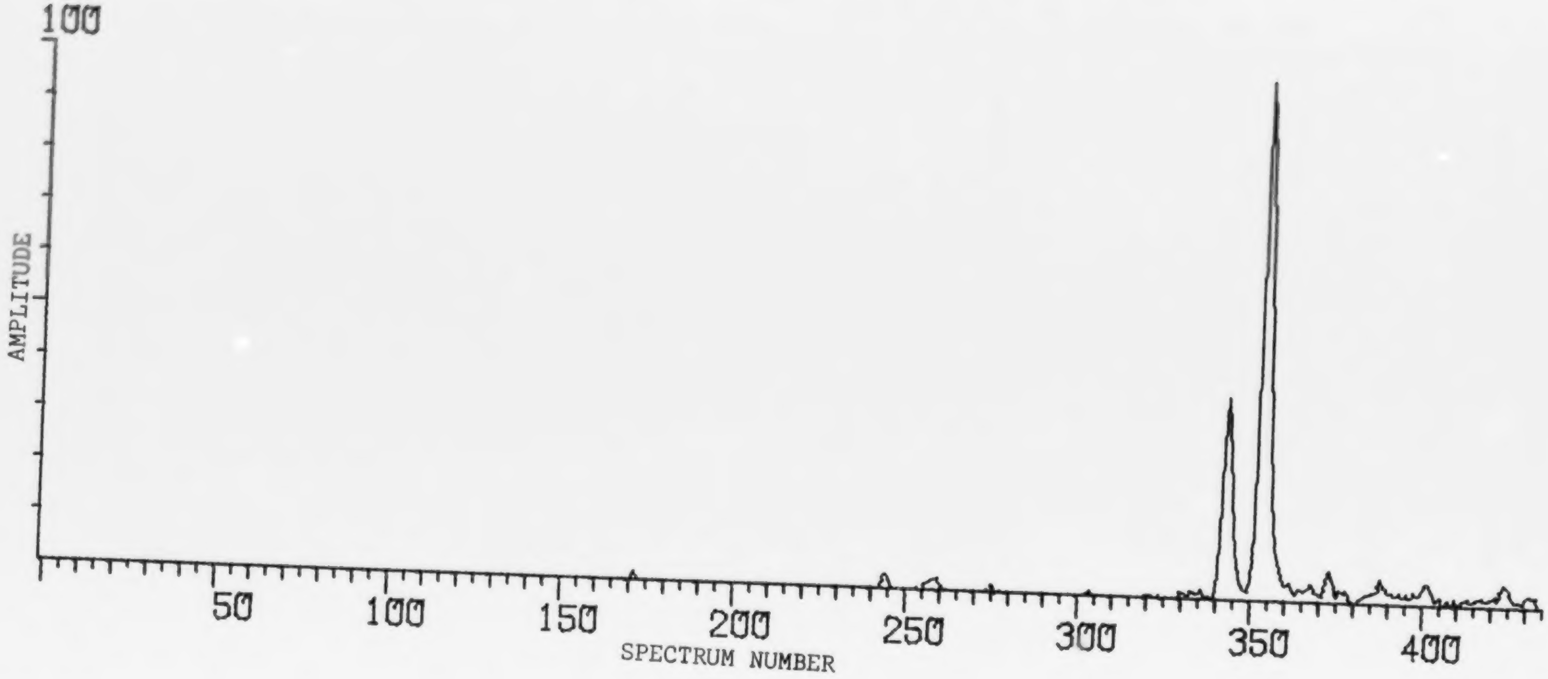


Figure 19. LMRGC of Methyl Chlorodehydroabietate M/Z 273

These two peaks locate the two isomers of methyl chlorodehydroabietate present in the sample.

A base-neutral extract of another sample from the Bergstrom Paper Company was sent to the U.S.EPA Environmental Research Laboratory in Athens, Georgia for additional identification and confirmation. The sample was analyzed on a 1.8 m column packed with OV-1 installed in a Varian MAT-44 GC/MS system equipped with the electron impact mode. The column was programmed from 50° to 250°C at 8°/min. The EPA laboratory confirmed about 15 compounds in the sample which we previously identified as aliphatic and aromatic hydrocarbons. Two of the compounds had a molecular ion of m/z 230. The mass spectra of these two compounds had isotopic molecular ions for one chlorine. One compound had a molecular ion of m/z 196. It apparently is the precursor of the above compounds (Appendix F). Future analysis by high resolution mass spectrometry at the EPA laboratory will help in its identification.

V. WASTE TREATMENT FACILITY DESCRIPTIONS

This section describes the pulp and paper mill and municipal waste treatment systems discharging to the Fox River. Dischargers are listed in downstream order. Table 2 following the treatment system descriptions gives mean BOD, suspended solids and flow data for 1977, taken from Wisconsin DNR NR 101 discharge reporting files.

PULP AND PAPER MILLS

Kimberly - Clark Corporation
Badger Globe and Neenah Paper Mill Divisions
Neenah, Wisconsin

The Badger Globe mill produces tissue wadding from purchased kraft pulp, and the Neenah Paper Mill produces fine business paper from purchased cotton sulfite pulp and produces rag pulp for its own use. An experimental mill, which is testing a tissue-forming machine, is located at Badger Globe. Process water is obtained from a well and from the Fox River. Fox River water is treated by sedimentation, flocculation, sand filters, and is chlorinated.

Process wastewaters from all mills are treated in a joint treatment system located at the Neenah Paper Mill Division.

Wastewater from the mills and waste discharge from the influent sand filter are pumped through a traveling screen and degritter to a jet aerated channel with 24-hour retention. Ammonia and phosphoric acid are added in the channel. From the channel, aerated effluent flows by gravity to the 105-foot clarifier located concentrically in the center of the channel. The clarifier effluent is then treated in a 76-foot polishing clarifier prior to discharge to the Fox River.

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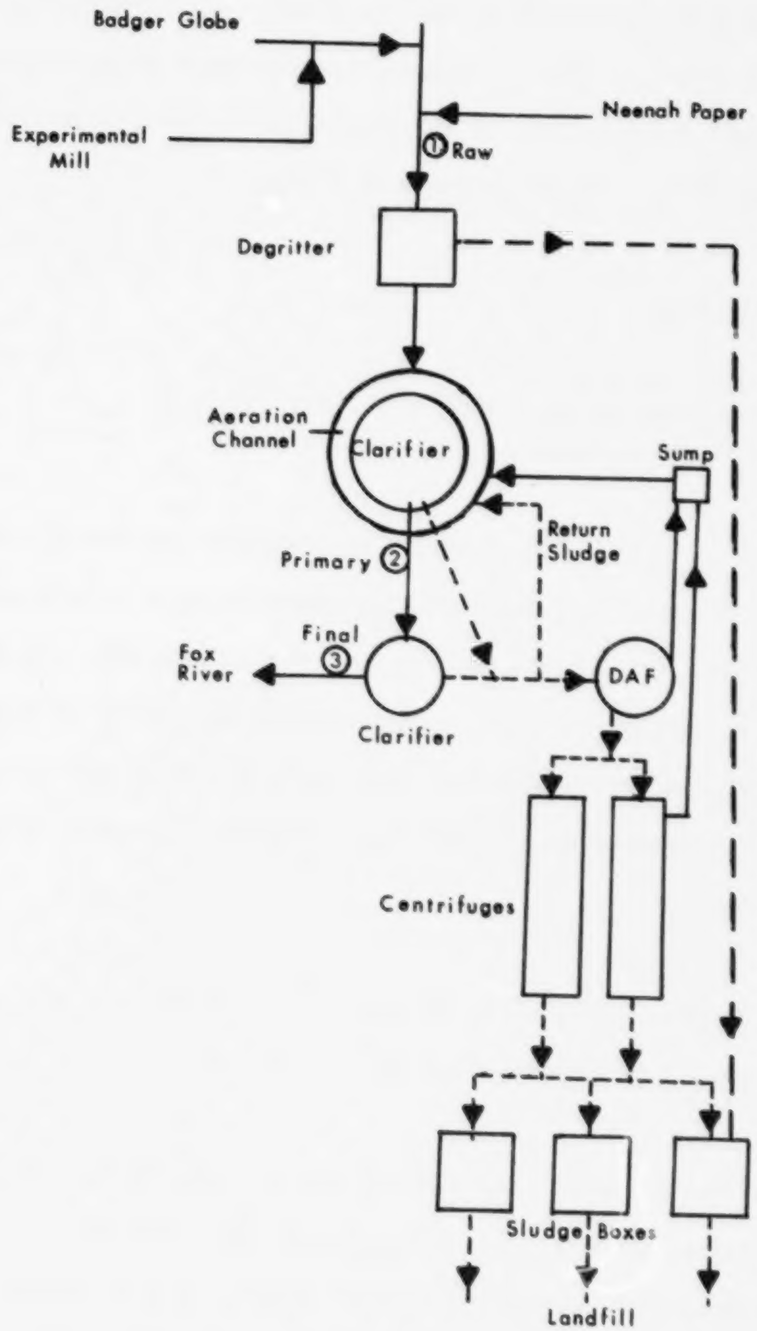
Badger Globe
Experimental Mill
Neenah Paper
① Raw
Degritter
Aeration Channel
Clarifier
Sump
Return Sludge
Primary ②
Final ③
Fox River
Clarifier
DAF
Centrifuges
Sludge Boxes
Landfill

Figure 20. Kimberly-Clark Badger Globe & Neenah Paper Waste Treatment System

Sludge from both clarifiers is thickened in a dissolved air flotation unit (DAF), pumped to centrifuges for dewatering, and then hauled to a landfill site. Centrate and excess flow from the DAF unit are returned to the jet-aerated channel. Polymer and alum are available if needed for coagulation and flocculation in the polishing clarifier, thickener, and centrifuges.

Bergstrom Paper Company
Neenah, Wisconsin

Bergstrom manufactures various grades of writing papers from reclaimed fiber and virgin pulp. The recycled material goes through a deinking process prior to blending with virgin pulp. The combined pulp is refined prior to sheet formation on one of three Fourdrinier machines.

Wastewaters generated in the deinking operation, paper production and process water treatment are directed to a 120-foot diameter primary clarifier, where chemicals are added to aid settling. The primary effluent is directed to a Zurn-Attisholz (Z-A) two stage biological treatment system. Waste-activated sludge is sent from the first storage aeration tank to an air flotation unit. The concentrated waste sludge is then pumped to the vacuum filter facility for dewatering prior to being hauled to the company landfill site. The air flotation effluent is returned to the first-stage aeration tank, and nutrients for the Z-A system are added to this stream. The Z-A system effluent is discharged through a parshall flume with a totalizer to Little Lake Butte des Morts. A refrigerated, flow-proportional, automatic sampler is used by the mill to collect effluent samples.

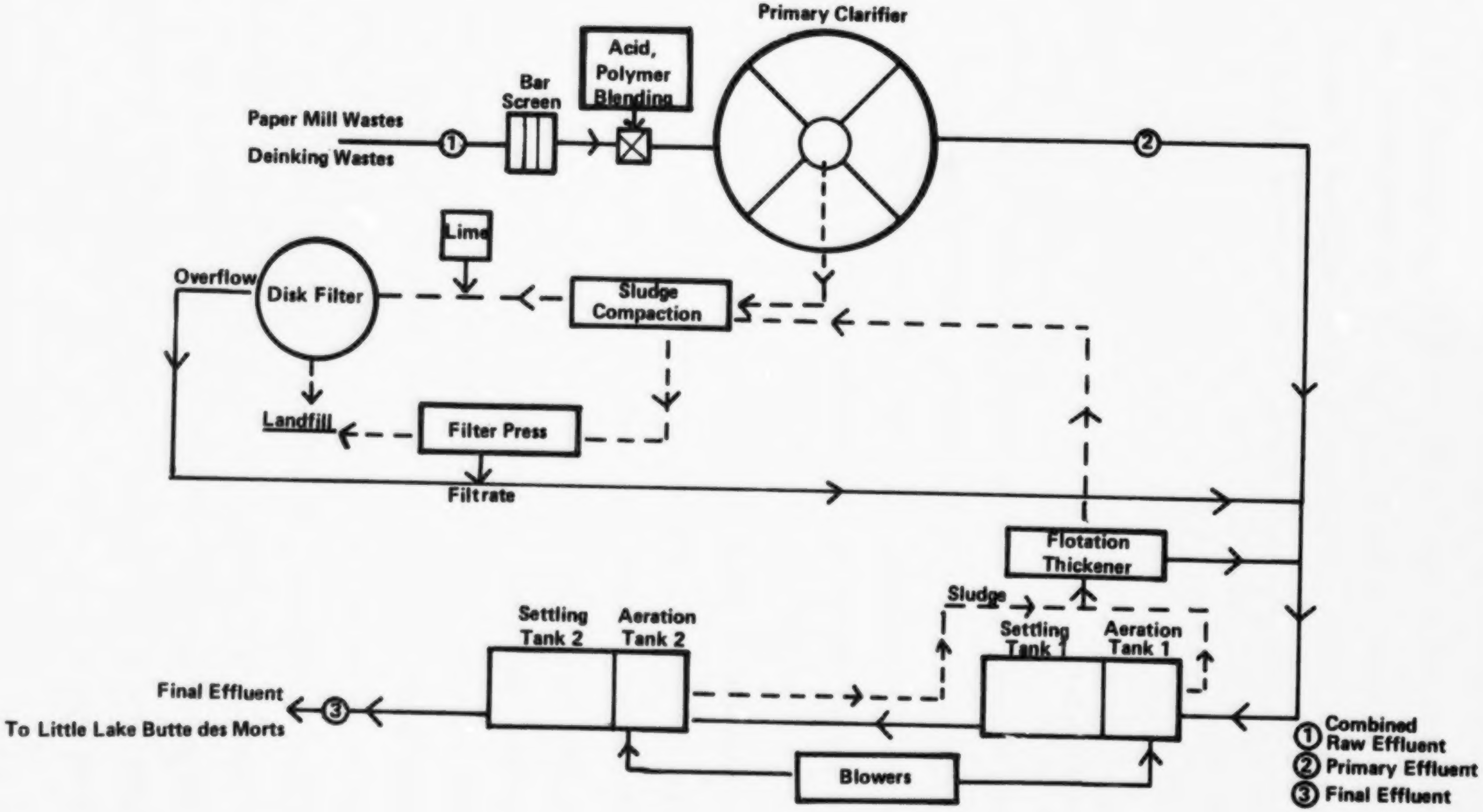
Primary Clarifier
Acid, Polymer Blending
Bar Screen
Paper Mill Wastes
Deinking Wastes
①
②
Lime
Overflow
Disk Filter
Sludge Compaction
Landfill
Filter Press
Filtrate
Flotation Thickener
Sludge
Settling Tank 1
Aeration Tank 1
Settling Tank 2
Aeration Tank 2
Final Effluent
To Little Lake Butte des Morts
③
Blowers
① Combined Raw Effluent
② Primary Effluent
③ Final Effluent

Figure 21. Bergstrom Paper Mill Waste Treatment System

For this study the mill's raw effluent, primary effluent, and final effluent were sampled as indicated on Figure 21.

Kimberly-Clark Corporation
Lakeview Mill
Neenah, Wisconsin

Kimberly-Clark Corporation (Lakeview Mill) manufactures sanitary tissue products from a furnish of 2/3 purchased virgin pulp and about 1/3 high-grade secondary fiber. Hydrapulpers are used to supply furnish to the five paper machines. Disk and drum savealls as well as DSM screens are used to reclaim fiber from white water prior to discharge to the waste treatment system. Process water is obtained from Little Lake Butte des Morts and from wells located on company property. Process water is clarified and chlorinated prior to use in the mill.

Process wastewaters are directed to a 125-foot clarifier. Additional inputs to the clarifier include sludges from the intake water treatment plant, raw water screen rejects, and centrate from the sludge presses and centrifuges. De-watered sludge is then hauled to a landfill site. A portion of the clarified effluent is returned to the mill for reuse and excess waste is discharged to Little Lake Butte des Morts.

Raw and final effluent samples were collected.

George A. Whiting Paper Company
Menasha, Wisconsin

The George Whiting Company manufactures approximately 20 tons per day of fine specialty paper from purchased kraft pulp on one paper machine. Process water is obtained from the City of Menasha.

Saveall overflows, boiler blowdown, and floor drainage are collected and pumped to a primary clarifier. The primary clarifier effluent is discharged to the Menasha Channel of the Fox River. Sludge from the clarifier is drawn off to a holding tank followed by polymer addition and dewatering on a centrifuge. Solids are hauled to a landfill site and centrate is returned to the clarifer.

Samples were obtained from the raw and final wastewater streams.

Wisconsin Tissue Mill
Menasha, Wisconsin

Wisconsin Tissue Mill produces napkins, placemats, table covers, and tray covers from purchased virgin pulp and reclaimed fiber. The recycled stock is deinked before it is blended with virgin pulp and is refined prior to formation of a sheet on one of two Fourdrinier machines.

Wastewater generated during deinking, pulp preparation, and paper production is directed through a mechanically cleaned bar screen and grit chamber before entering the 70-foot primary clarifier. Polymers and bentonite are added to the wastewater prior to discharge to the primary clarifier for coagulation. Primary clarifier effluent is pumped to a Zurn-Attosholz (Z-A) two-stage activated sludge secondary treatment system after addition of phosphoric acid. The secondary treatment effluent is directed to a 52-foot storage reservoir from which a portion of the final effluent is reused by the mill and excess flow is discharged to the Fox River.

Solids removed by the primary and secondary treatment systems are directed to a 52-foot gravity thickener where chlorine is added to retard decomposition and prevent odor problems. The thickened sludge is dewatered, after polymer addition, on two centrifuges. The dewatered sludge is hauled to a sanitary landfill. Centrate and thickener overflow are returned to the influent wet well.

For this study samples were collected of the raw, primary, and final effluents as indicated on Figure 22.

Riverside Paper
Appleton, Wisconsin

Riverside Paper manufactures book, bond, and construction paper from deinked and purchased virgin pulp. Approximately 75 percent of the paper is made from secondary fibers, a major portion of which come from papers having wax coatings. The wax is removed in a trichlorethylene solvent extraction process prior to the normal deinking operation. Spent solvent is directed to a still and condenser to remove wax and polyethylene. The secondary fiber is then screened, thickened, and bleached prior to use in the mill. Process water is obtained from the Fox River and is treated with alum and chlorine. Water treatment plant sludge is discharged to the Appleton municipal sanitary sewer.

The two paper machines in the mill are equipped with savealls to recycle fiber back into the process. Clear water from the savealls is discharged to the Fox River. Wastewater from the deinking process and other sources is discharged to the municipal sanitary sewer.

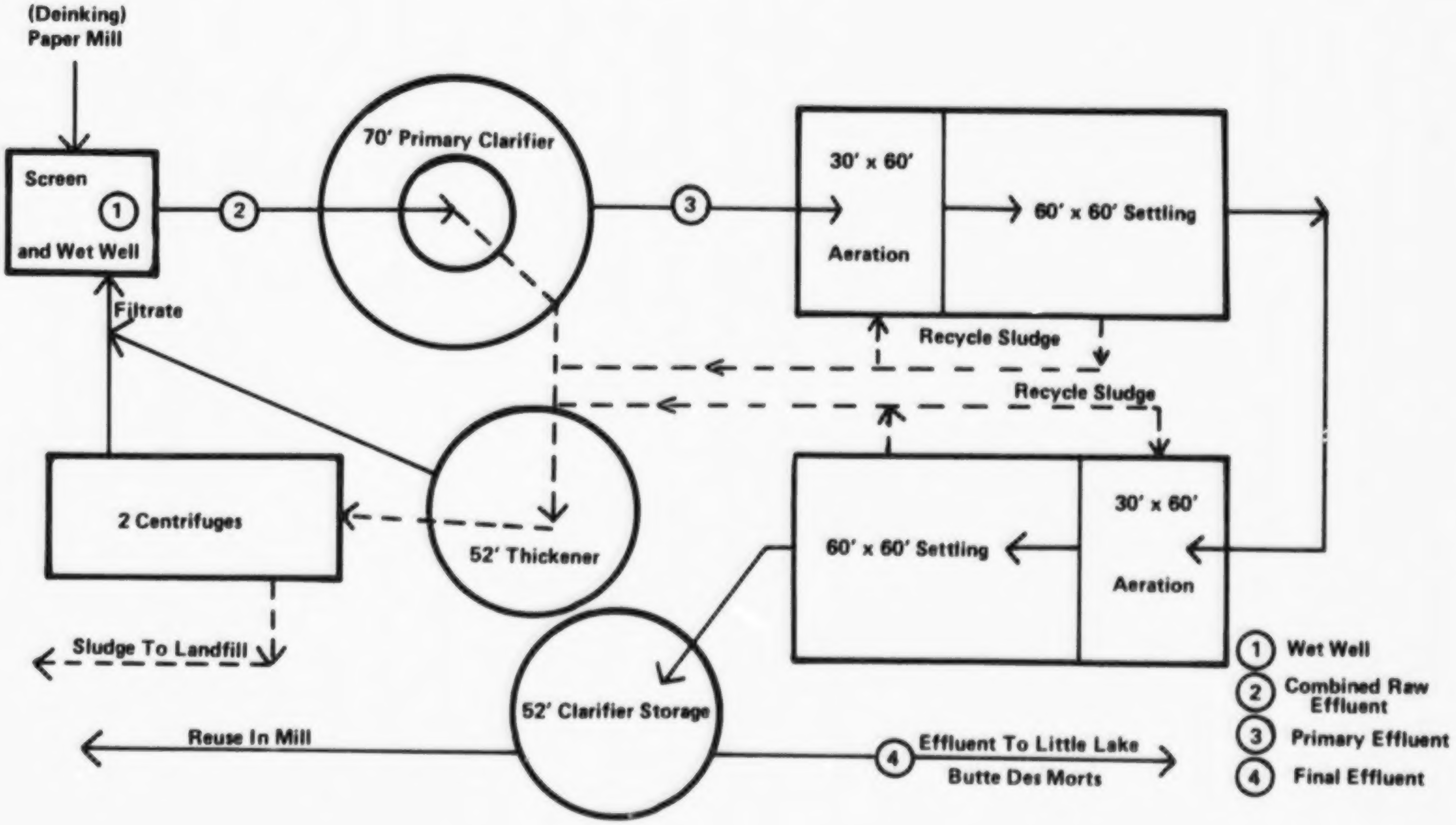
(Deinking) Paper Mill
Screen
①
and Wet Well
②
70' Primary Clarifier
③
30' x 60'
Aeration
60' x 60' Settling
Recycle Sludge
Recycle Sludge
Filtrate
2 Centrifuges
52' Thickener
30' x 60'
Aeration
60' x 60' Settling
Sludge To Landfill
52' Clarifier Storage
Reuse In Mill
④
Effluent To Little Lake Butte Des Morts
① Wet Well
② Combined Raw Effluent
③ Primary Effluent
④ Final Effluent

Figure 22. Wisconsin Tissue Mill Waste Treatment System

For this study a sample was collected from the discharge to the Fox River.

Consolidated Papers, Incorporated
Appleton, Wisconsin

Consolidated Papers, Incorporated at Appleton produces an annual average of 189 tons a day of bleached sulfite pulp from purchased wood chips. Chlorine is the principal bleaching agent. Calcium bisulfite cooking acid is produced on site. The pulp is produced in nine digesters with the cooking acid. This process is followed by screening, fractioning, washing, bleaching, and further washing prior to sheet formation on a vacuum cylinder machine. Lap (wet sheet) pulp is the final product from the mill. Spent sulfite liquor is evaporated and processed into spray dried products at a plant adjacent to the mill.

Process water is obtained from the Fox River and is treated in an accelerator with additions of alum, chlorine, and polymers. The main mill sewer carries wastes from floor drains, accelerator sludge, evaporator plant condensate, bleach plant washwater, and other mill wastewaters and discharges to the Fox River. There was no external waste treatment during the investigation.

Samples were collected from the intake water and from the process waste final effluent.

Midtec Paper Corporation
Kimberly, Wisconsin

Midtec Paper Corporation manufactures groundwood pulp and coated fine paper from groundwood and purchased bleached kraft pulp. Five Fourdrinier paper machines and an off-machine coater are used for paper production. The majority of process water is obtained from the Fox River and treated either in a sedimentation basin plus sand filters or in an accelerator. Incoming water is chlorinated and process water is occasionally chlorinated for slime control. At the time of the survey, the company operated a primary wastewater treatment system consisting of primary clarification, sludge thickening, sludge centrifuging, and land disposal. Mill effluent was pumped to a grit chamber where grit, screenings, and trash were dewatered and conveyed to a container for disposal as solid waste. From the grit chamber waste flowed to two 135-foot primary clarifiers. Clarified effluent was discharged to the Fox River and sludge was pumped to a 65-foot sludge thickener. Sludge from the thickener flowed to two centrifuges, where it was dewatered and hauled to a landfill site. Centrate was returned to the grit chamber.

The system was upgraded in December, 1977 by the addition of a jet aeration system ahead of the clarifier for biological oxidation. A third centrifuge has also been added to increase dewatering capacity.

Samples were collected from the raw mill effluent and final effluent discharged to the Fox River. Sample locations are indicated on Figure 23.

NCR Appleton Papers
Combined Locks, Wisconsin

Appleton Papers manufactures NCR and telephone directory paper from blends of purchased and chemi-mechanical manufactured pulp, and secondary fibers. A portion of the pulp is bleached with hydrogen peroxide prior

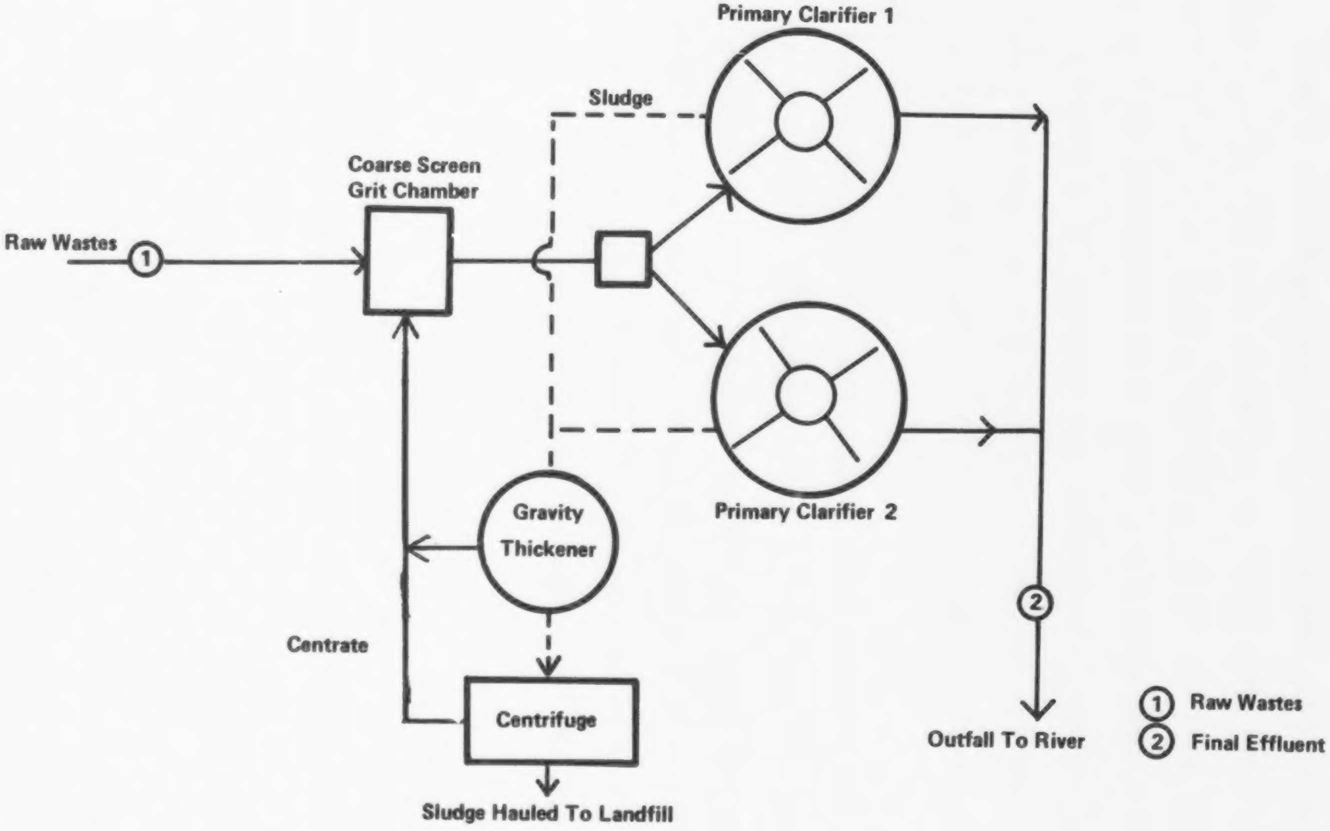
Primary Clarifier 1
Sludge
Coarse Screen
Grit Chamber
Raw Wastes
①
Primary Clarifier 2
Gravity
Thickener
Centrate
Centrifuge
Sludge Hauled To Landfill
②
Outfall To River
① Raw Wastes
② Final Effluent

Figure 23. Midtec Paper Corp. Waste Treatment System

to use on one of the paper machines. Spent liquor from the chemi-mechanical pulping process is discharged to an incineration system (copeland process) that consists of liquor and concentrated liquor holding tanks, evaporator, fluidized bed reactor, and scrubber. Process wastewaters are collected and passed through a rough screening facility prior to being pumped, along with effluent from the copeland facility, to two 80-foot diameter primary clarifiers operating in parallel. Solids are dewatered on two vacuum filters, after which they are hauled to the company landfill site. Filtrate is returned to the clarifier.

Effluent from the twin clarifiers is pumped to an oxygen reactor system (Unox) for final treatment. High purity oxygen flows into the three-stage aeration tank along with primary treatment effluent. The tank is covered to retain gaseous oxygen and maintain positive pressure to ensure forward flow to the tank and avoid back-mixing from stage to stage. Nutrients are fed to the influent in the form of ammonia and phosphoric acid.

From the reactor, flow is to the clarifier, from which sludge flows to a vacuum filter for dewatering and clarified effluent is discharged to the Fox River. Effluent from the vacuum filter is returned to the Unox reactor influent.

Samples were collected from the raw effluent, primary effluent, and final effluent to the Fox River. Sampling points are illustrated on Figure 24.

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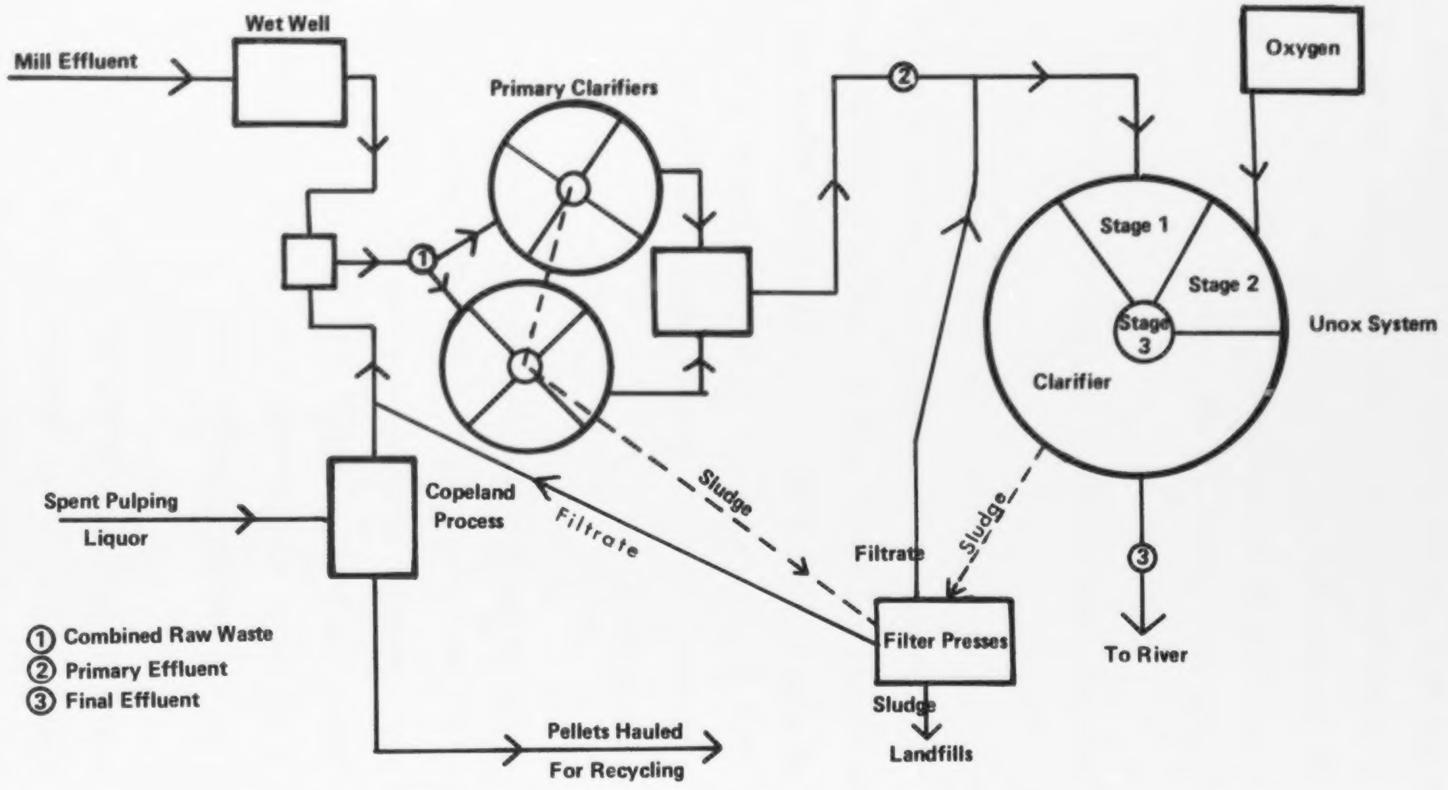
Mill Effluent
Wet Well
Primary Clarifiers
Spent Pulping Liquor
Copeland Process
Filtrate
Sludge
①
②
③
Oxygen
Stage 1
Stage 2
Stage 3
Clarifier
Unox System
Sludge
Filtrate
Filter Presses
Sludge
Landfills
To River
Pellets Hauled For Recycling
① Combined Raw Waste
② Primary Effluent
③ Final Effluent

Figure 24. NCR, Appleton Paper Division Waste Treatment System

Thilmany
Kaukauna, Wisconsin

The Thilmany Pulp and Paper Company produces about 431 tons a day of unbleached kraft pulp and 581 tons a day of specialty papers. On May 16, 1977 additional effluent treatment was put on line to handle all of the plant's waste. Because samples were collected before and after the new equipment installation, both systems are described.

The previous effluent treatment system is illustrated by Figure 25.

Process wastewaters from the pulping operation were directed through a sewer equipped with a Parshall flume and meter for flow determination. An automatic sampler collected unrefrigerated, nonflow proportion samples. Phosphoric acid and ammonia were added as nutrient sources before the effluent was lifted to an aerated lagoon. This lagoon had about a 7.7-day retention time at design flow. As many as seven 40 hp floating aerators kept the lagoon mixed.

Process wastewater from the paper mill plus sludges generated in the raw water treatment process were discharged to a 185 foot-diameter clarifier. A Parshall flume with integrator meter measured the flow. Samples were collected by a refrigerated, nonflow proportional automatic sampler. The sludge from the clarifier was dewatered in a pressure filter and solids were hauled to the company's landfill site.

Both the aerated lagoon and clarifier discharged to a second lagoon, which was not aerated and had a 1.3-day retention time at design flow. The combined effluent was discharged from the second lagoon to the Fox River via a submerged outfall. Flow measurement and automatic sampling

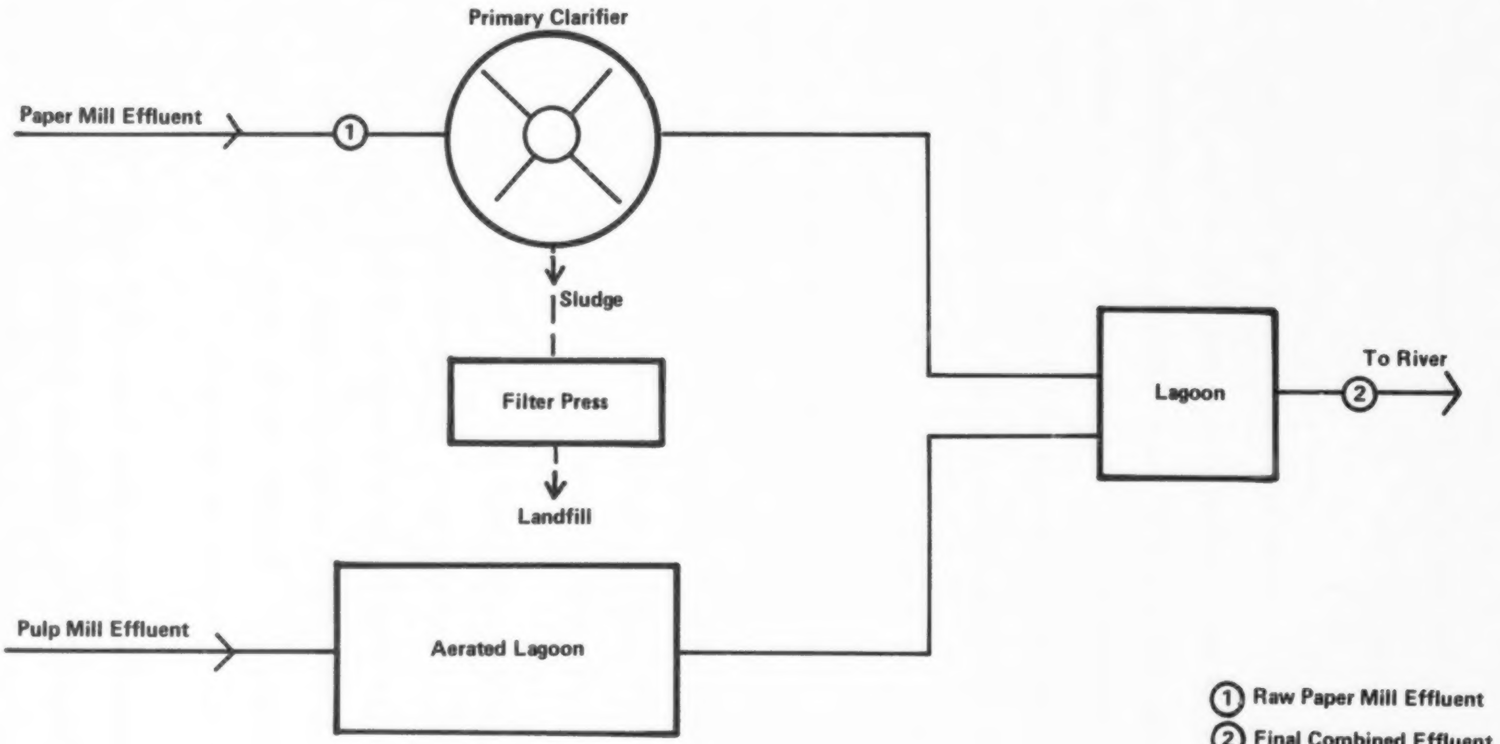
Primary Clarifier
Paper Mill Effluent
1
Sludge
Filter Press
Landfill
Pulp Mill Effluent
Aerated Lagoon
Lagoon
To River
2
① Raw Paper Mill Effluent
② Final Combined Effluent

Figure 25. Thilmany Pulp & Paper Waste Treatment System (before May 16, 1977)

took place prior to final discharge. The automatic sampler was not refrigerated or flow proportional.

Samples of raw paper mill waste and final effluent were collected from this system as shown on Figure 25.

The present treatment system is shown on Figure 26. Expansion of the effluent treatment facility consisted of a nutrient feed system, UNOX oxygen dissolution system complete with oxygen generator, liquid oxygen storage, and secondary clarification. Proportional refrigerated samplers are located to collect samples of the main mill sewer, pulp mill effluent, combined effluents with nutrients before the UNOX system, and the final clarifier effluent line.

During normal operation, paper mill waste flows by gravity through a bar screen and is then pumped to a primary clarifier for removal of suspended solids. Solids are dewatered by a pressure filter and are disposed of at a landfill. Clarified effluent flows by gravity to the UNOX reactor after being combined with aerated lagoon effluent and nutrients.

Pulp mill waste, after ammonia and phosphoric acid nutrients are added, flows through a bar rack and is raised to the aerated lagoon. Up to nine floating aerators, located in the approximate 10-day detention lagoon aid removal of biodegradable materials. Pumps raise the aerated lagoon effluents for transfer to the UNOX reactor after being combined with the primary clarifier effluent and nutrients.

The combined primary clarifier and aerated lagoon effluents, together with sufficient recycled biological solids to maintain a mixed liquor suspended solids (MLSS) concentration of about 4,800 mg/L, are introduced

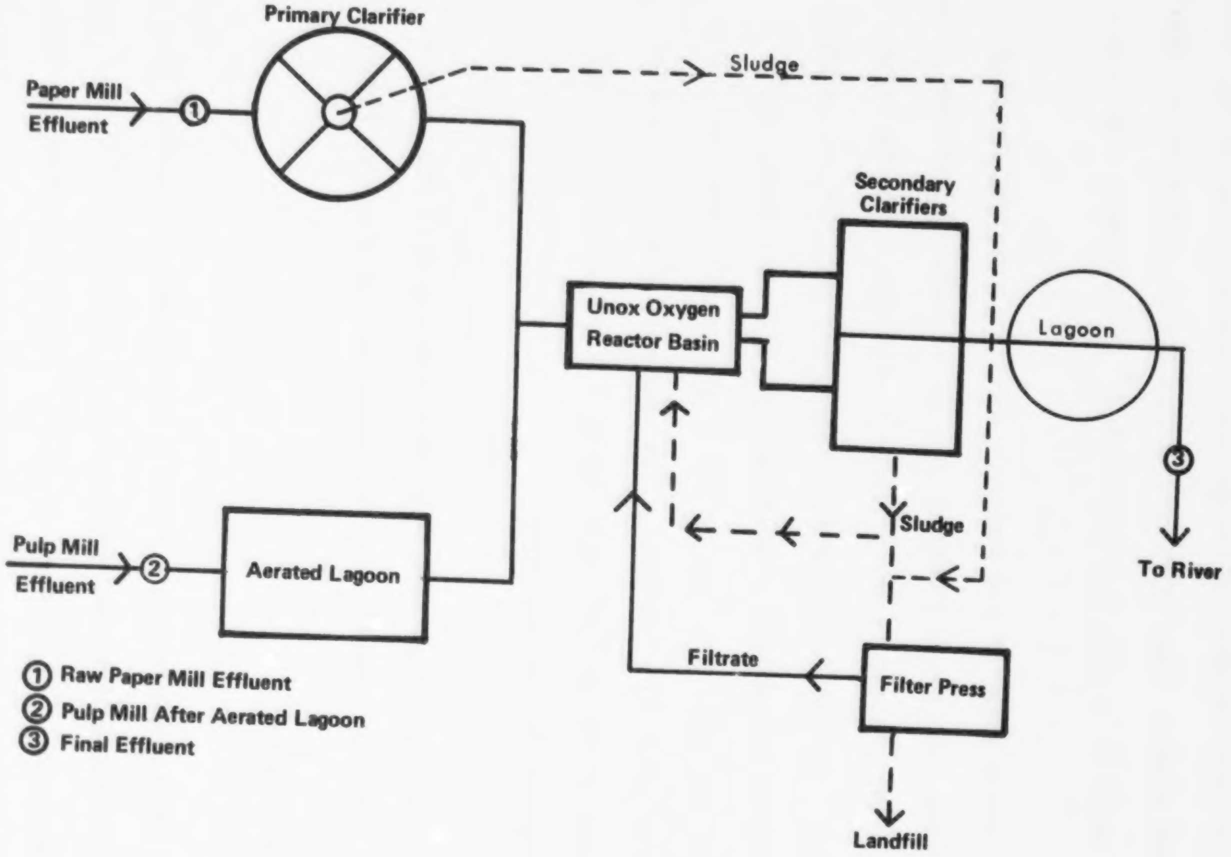
Primary Clarifier
Sludge
Paper Mill Effluent
①
Secondary Clarifiers
Unox Oxygen Reactor Basin
Lagoon
③
Sludge
To River
Pulp Mill Effluent
②
Aerated Lagoon
Filtrate
Filter Press
Landfill
① Raw Paper Mill Effluent
② Pulp Mill After Aerated Lagoon
③ Final Effluent

Figure 26. Thilmany Pulp & Paper Waste Treatment System (after May 16, 1977)

into the first stage of the UNOX reactor. Sufficient oxygen (90 percent purity) to satisfy the BOD is also introduced into the first stage. The oxygen is supplied by a 14-ton 2-day oxygen generating system. Surface aerators assure mass transfer of oxygen and adequate mixing in the first and subsequent stages. The liquid and active solids remain in the UNOX reactor for about 45 minutes and then flow to the secondary clarifiers.

A flow distributor ahead of the secondary clarifier divides the UNOX reactor effluent flow equally between the two secondary clarifiers. The biological solids present in the influent stream settle to the bottom of the clarifiers. Sufficient biological solids are recycled to the UNOX reactor to assure proper MLSS concentrations, with the excess being combined with the primary solids in the sludge tanks. These solids are dewatered and hauled to a landfill. The secondary clarifier-treated effluent flows to the second lagoon (about 1.5 days retention time) prior to discharge to the Fox River.

Samples from the new system were collected from the mill raw, aerated lagoon, and final effluents. Sampling locations are shown on Figure 26.

Nicolet Paper Company
De Pere, Wisconsin

The Nicolet Paper Company manufactures glassine and grease-proof specialty paper from purchased kraft and sulfite pulp. After repulping and refining, the sheet is formed on one of four Fourdrinier paper machines. All paper machines are equipped with flotation savealls. Process water is obtained from the Fox River.

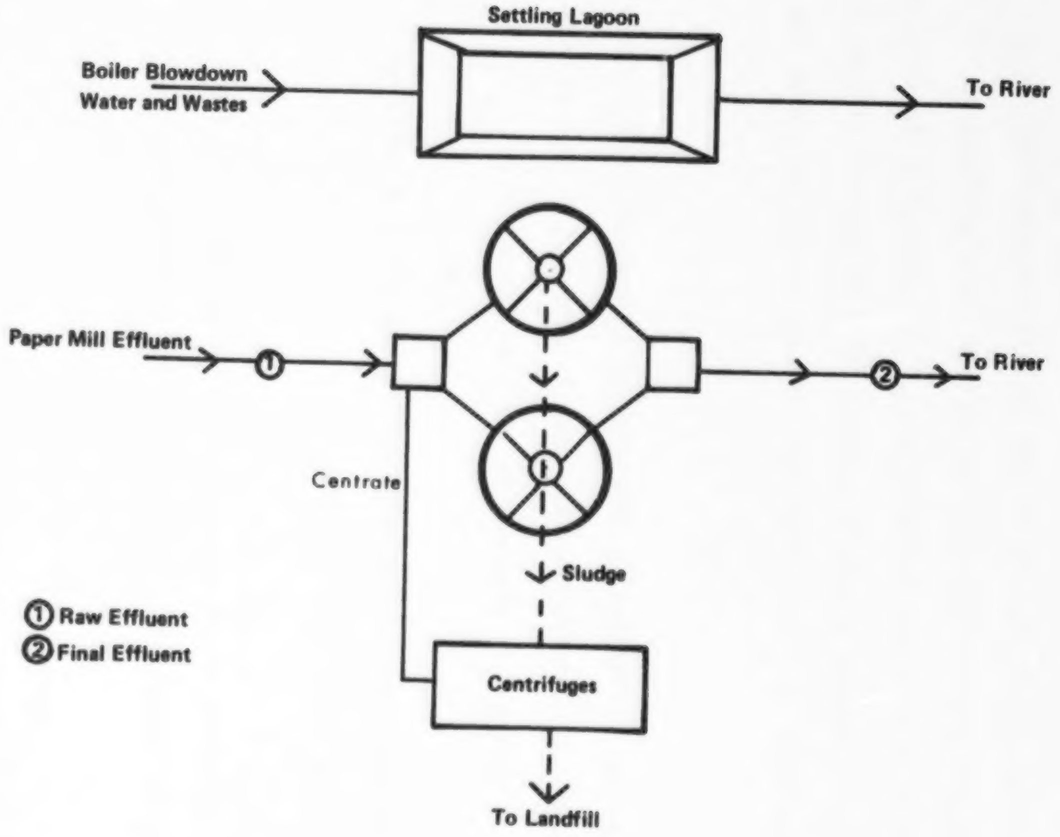
Settling Lagoon
Boiler Blowdown
Water and Wastes
To River
Paper Mill Effluent
①
②
To River
Centrate
Sludge
Centrifuges
To Landfill
① Raw Effluent
② Final Effluent

Figure 27. Nicolet Paper Co. Waste Treatment System

Process wastewaters from the papermaking operation and all of the sludge generated in the water treatment plant are directed to the waste treatment plant through a 14-inch force main. Each of the three lift stations in the mill is equipped with an emergency overflow to the Fox River. During sample collections no discharges occurred from these overflows, but they are used occasionally.

The waste treatment plant consists of two 56-foot diameter clarifiers and sludge dewatering centrifuges. Flow through the clarifiers is measured by means of a magnetic flow meter and is recorded on an integrator totalizer. A refrigerated automatic sampler collects samples of clarifier effluent proportional to flow. Clarified effluent is discharged to the Fox River.

Sludge from the two clarifiers is dewatered to approximately 15 percent solids in one of two centrifuges. The cake is disposed of by a private contractor, and centrate is returned to the clarifier.

Boiler blowdown and some cooling water are discharged to a settling lagoon adjacent to the treatment plant.

Samples were collected of the raw effluent from the mill, and final effluent from the treatment system as indicated on Figure 27.

Fort Howard Paper Company
Green Bay, Wisconsin

Fort Howard Paper Company manufactures various tissue products from reclaimed secondary fiber and purchased virgin pulp. The reclaimed fiber is washed, bleached, combined with virgin pulp, and refined prior to sheet formation on one of the company's nine paper machines. Process water is obtained from the Fox River and is clarified and chlorinated prior to use.

The wastewater treatment system is composed of a primary clarifier for paper mill wastes, settling and aeration lagoons, and secondary clarifier for deinking wastes. Deinking wastes are directed to one or two of the five settling lagoons for solids separation. The remaining lagoons are at some stage of dewatering. The lagoons are operated on a rotation basis,and a lagoon completes its cycle in 4 to 6 weeks.

Settling lagoon effluent then flows into three mechanically aerated basins. Nutrient addition to the mixed liquor is accomplished by adding ammonia to the aeration basin influent and phosphoric acid to the return activated sludge. Effluent from the aeration basins flows to the 180-foot deinking final clarifier. Final clarifier effluent is then combined with effluent from the 180-foot mill clarifier and discharged to the Fox River.

Sludge from the mill and deinking clarifiers is pumped to conditioning tanks,where lime and calcium hypochlorite are introduced. The combined sludges are then directed to the settling lagoons and are ultimately removed to a landfill site.

Samples were collected only from Fort Howard's final effluent. The treatment system and sampling location are indicated on Figure 28.

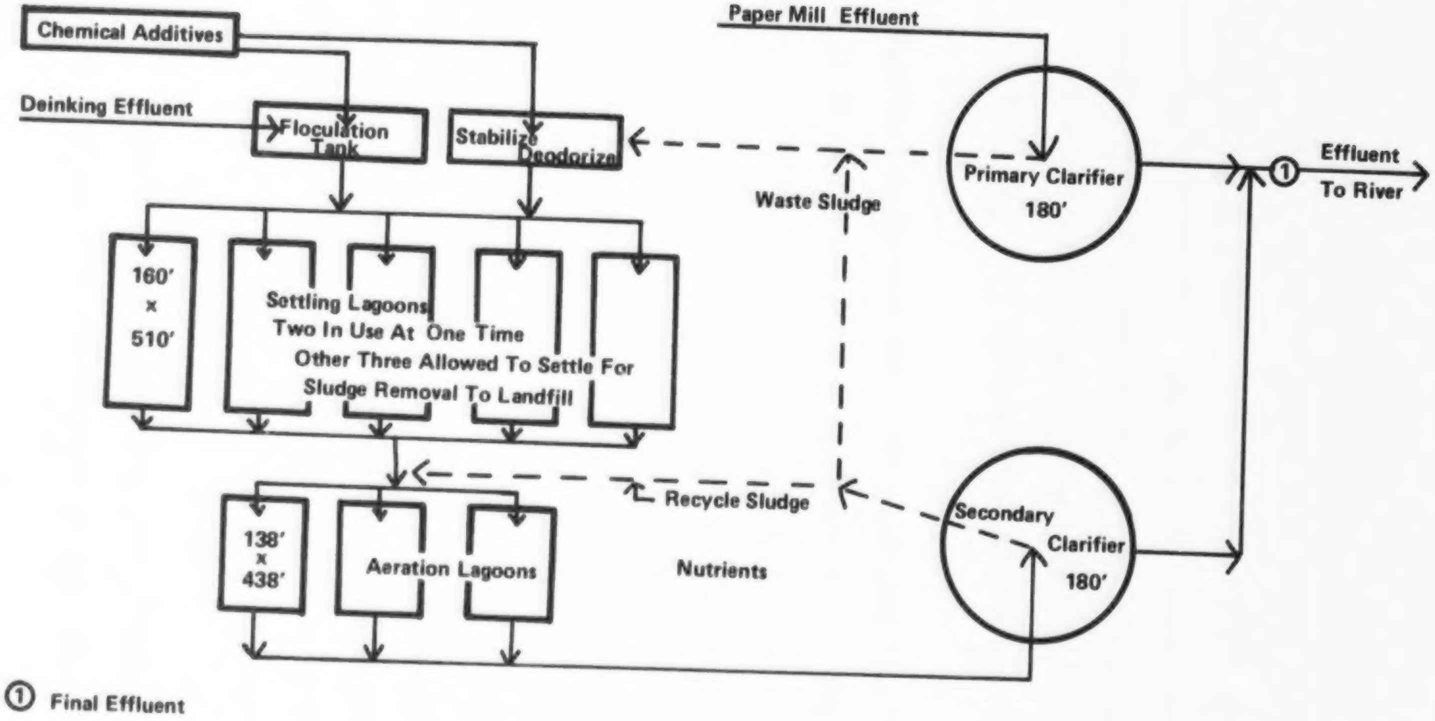
Chemical Additives
Deinking Effluent
Floculation Tank
Stabilize Deodorize
Paper Mill Effluent
Primary Clarifier 180'
Effluent
To River
①
Waste Sludge
160' x 510'
Settling Lagoons Two In Use At One Time Other Three Allowed To Settle For Sludge Removal To Landfill
Recycle Sludge
138' x 438'
Aeration Lagoons
Nutrients
Secondary Clarifier 180'
① Final Effluent

Figure 28. Fort Howard Paper Co. Waste Treatment System

American Can Company
Green Bay, Wisconsin

American Can manufactures tissue products from calcium-base sulphite pulp and purchased pulp. Cooking acid is produced on site and is supplied to four digesters, along with chips and steam. Following digestion the pulp is bleached and refined prior to sheet formation on one of six paper machines. Process water is obtained from the Fox River and is clarified and chlorinated prior to use.

Excess paper machine whitewater, water treatment sludges, and boiler house wastewaters are directed to one of three lagoons. One lagoon is always in use while the others are being dewatered for solids removal to a landfill site. Effluent from the lagoons is discharged to the Fox River.

Other wastes--consisting of spent sulphite liquor, solids rejects, and bleach liquor making, spray drying, and digester area losses--are directed to the Green Bay Metropolitan Sewerage District.

Samples were collected of the raw effluent discharged to the lagoons and the final effluent from the lagoons, which is discharged to the Fox River.

Proctor & Gamble Paper Products
Green Bay, Wisconsin

Proctor & Gamble Paper Products manufactures various tissue products from ammonia-base sulphite pulp and purchased pulp. Pulp and paper production averages about 1,000 tons a day. Cooking acid is produced on site and is supplied to the digesters, along with chips and steam. Following digestion the pulp is cleaned, bleached, and refined prior to sheet formation. Process water is obtained from the Fox River and is clarified and chlorinated prior to use.

Sludge from the process water clarifier is thickened in an air floatation unit, mixed with particulate scrubber solids, and centrifuged prior to disposal by a private contractor. Excess whitewater and final effluent are discharged to the Fox River. Other wastewater, consisting of whitewater and losses from the pulp mill and paper machines, is directed to the Green Bay Metropolitan Sewerage District.

Samples were collected from the final effluent discharged to the Green Bay sewage district and from the process water intake.

Green Bay Packaging
Green Bay, Wisconsin

Green Bay Packaging produces about 300 tons a day of corrugating medium from neutral sulfite semichemical pulp, and repulped waste corrugated boxes and clippings. Process water is obtained from Green Bay and the Fox River.

The mill operates with an essentially closed whitewater system. Excess water is removed from the system by a reverse osmosis (RO) plant. Wastes from the whitewater system are fed to the RO unit and are separated into uncontaminated water (permeate) and a concentrate of whitewater solubles, which is returned to the countercurrent washing system in the pulp mill. Feed to the RO plant contains 4 to 6 percent dissolved solids consisting of wood extractives and sodium lignosulfonates. After passage through the RO unit, a portion of the concentrate is returned to the pulp mill and the remainder is recycled for combining with fresh feed. Permeate is discharged to the Fox River. Figure 29 is a schematic of the treatment system including the sample location.

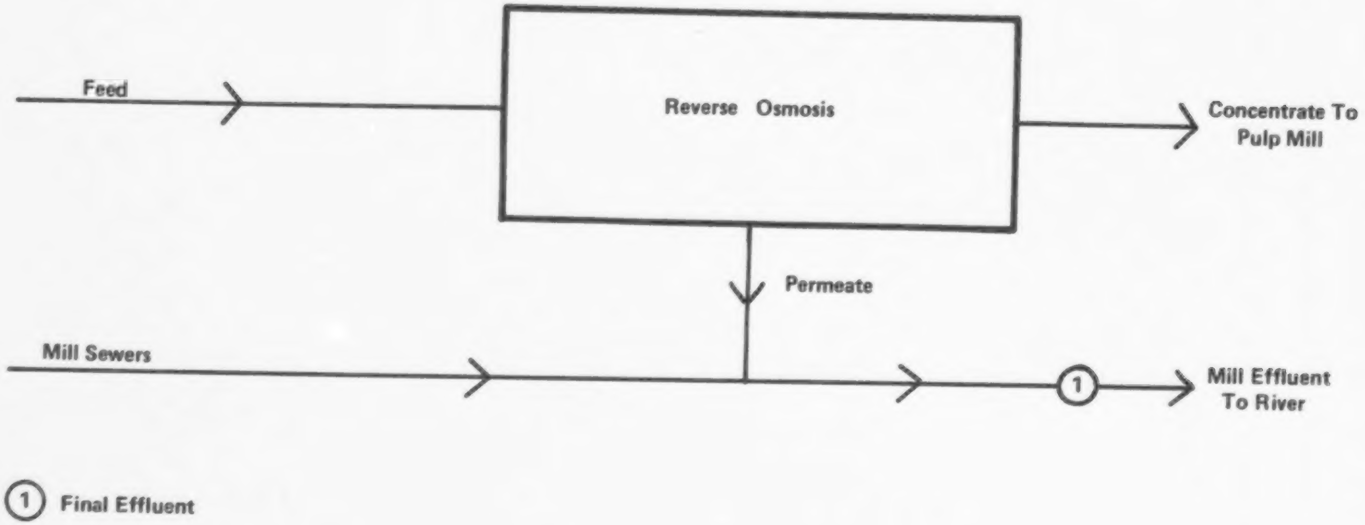
Feed
Reverse Osmosis
Concentrate To Pulp Mill
Permeate
Mill Sewers
1
Mill Effluent To River
1 Final Effluent

Figure 29. Green Bay Packaging Waste Treatment System

Neenah-Menasha Sewerage Commission
Menasha, Wisconsin

The Neenah-Menasha Sewerage Commission operates an activated sludge type sewage treatment plant serving a population of about 39,000 people. The plant consists of three 75-foot primary clarifiers, two aeration channels, and two 120-foot secondary clarifiers. Raw wastewater enters the system through a barscreen and wet well and then flows to the primary clarifiers, which receive a portion of the activated sludge from the final clarifiers. Primary clarifier effluent flows to the duel aeration channels, which also receive activated sludge. Aeration channel effluent flows to the two final clarifiers. Effluent from the final clarifiers is then chlorinated before discharge to the lower end of the North Menasha channel at the head of Little Lake Butte des Morts.

Excess activated sludge and primary clarifier sludge is pumped to a holding tank, flotation, and vacuum filter system. Filtrate is returned to the raw influent and filter cake is incinerated. Figure 30 is a diagram of the treatment facility and sampling locations.

Town of Menasha Sanitary District (East)
Menasha, Wisconsin

The Town of Menasha, East Side Sewage Treatment Plant utilizes dual activated sludge contact stabilization tanks for secondary treatment. The plant serves a population of about 6,500 and consists of a comminutor, contact aeration, settling basin, reaeration, and aerobic digestion in twin units followed by chlorination. Sludge is hauled to a landfill or

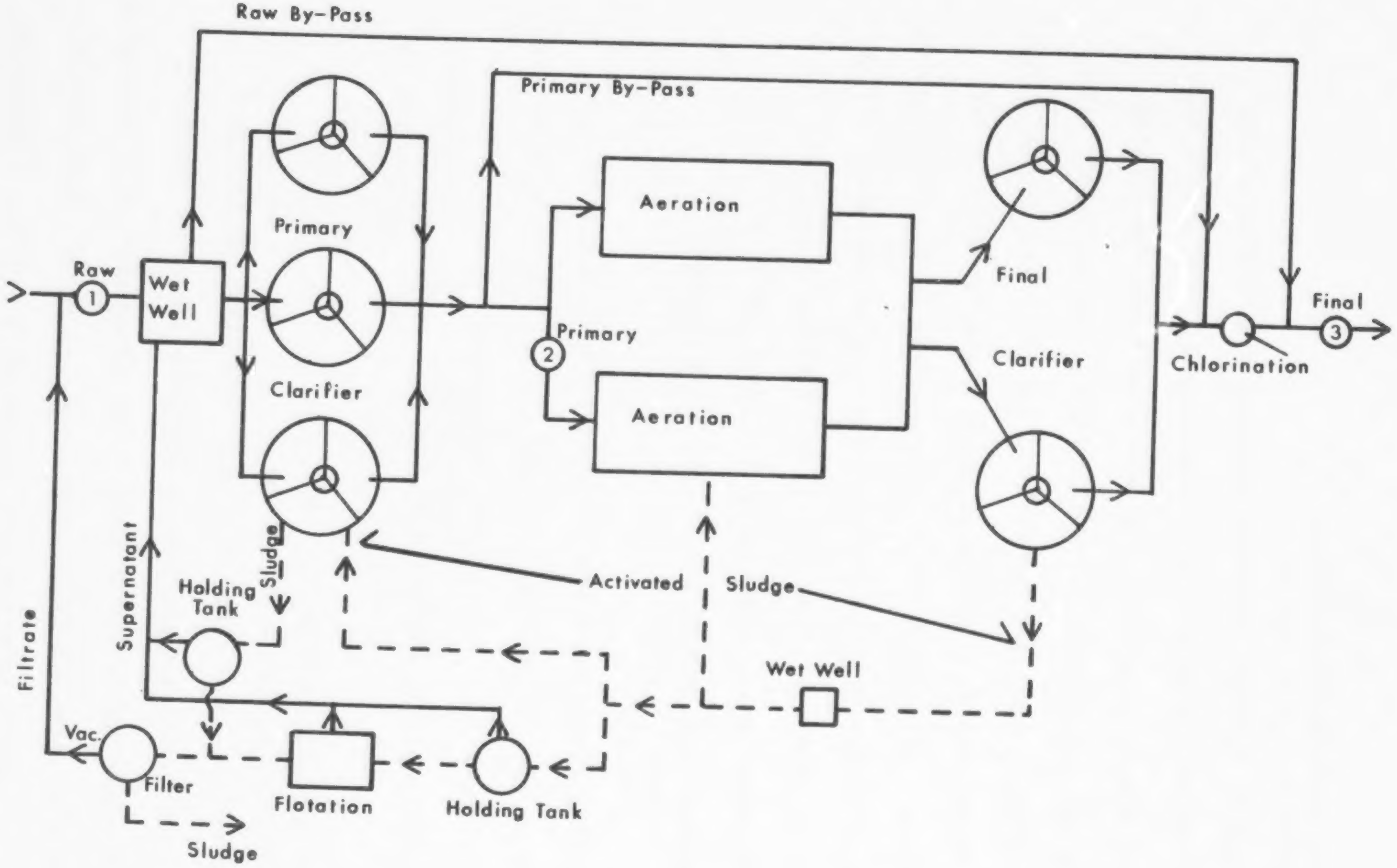
Raw By-Pass
Primary By-Pass
Raw
1
Wet Well
Primary
Clarifier
2
Primary
Aeration
Aeration
Final
Clarifier
Chlorination
Final
3
Sludge
Holding Tank
Supernatant
Filtrate
Activated
Sludge
Wet Well
Vac.
Filter
Flotation
Holding Tank
Sludge

Figure 30. Neenah-Menasha Sewage Treatment System

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farm fields in the area. Effluent is discharged to Little Lake Butte des Morts.

Town of Menasha, Sanitary District No. 4 (West)
Neenah, Wisconsin

The existing sewage treatment plant utilizes contact stabilization for secondary treatment. The plant consists of a comminutor, lift station, contact aeration, settling basin, reaeration, aerobic digestion, and chlorination. The plant discharges to Little Lake Butte des Morts, and a compliance monitoring survey conducted in May, 1977 indicates the plant operates efficiently under normal flow. The plant had a high chlorine residual when surveyed.

Butte des Morts Utility District
Appleton, Wisconsin

The Butte des Morts Utility District Sewage Treatment Plant consists of a barminutor, contact stabilization activated sludge unit, and clarifier. Effluent from the clarifier is chlorinated prior to discharge to Mud Creek a short distance from its junction with the Fox River. Liquid alum is added near the clarifier inlet for phosphorus removal. Digester sludge flows to a lagoon and is hauled from there to a landfill or to agricultural fields in the area. Major industries discharging to the plant include Rich Products (bakery grease) and Fox Operations (painting waste). Final effluent samples were collected.

Appleton Sewage Treatment Plant
Appleton, Wisconsin

The City of Appleton operates an activated sludge-type sewage treatment plant that was placed in operation in 1964. During this survey the plant was in process of expansion. The facility serves a population of about 58,000, and the following significant industries discharge to the facility: Fox River Paper Company, Riverside Paper Company, NCR Appleton Papers, Appleton Mills, Stokely Van Camp, Consolidated Badger Co-op, and Foremost Food.

The treatment plant consists of the following: solids grinding and degritting, four primary clarifiers, four aeration basins with installed piping for various operational modes, two final clarifiers, and chlorine contact tank for effluent disinfection prior to discharge to the Fox River. About 400 lbs a day of chlorine is used for disinfection of final effluent and about 300 lbs a day is used on outfall 002, which discharages primary effluent. Solids collected from the primary and final clarifiers are anaerobically digested prior to dewatering by vacuum filtration. Dewatered solids are hauled to a landfill site.

Phosphorus removal is achieved by precipitation, using ferric chloride added as a conditioner in the sludge dewatering process. Additional amounts of ferric chloride are added at the plant intake and aeration basin effluent. In addition, polymer is added to the raw sewage to aid in primary clarifier settling. Figure 31 is a diagram of the facility and sampling locations.

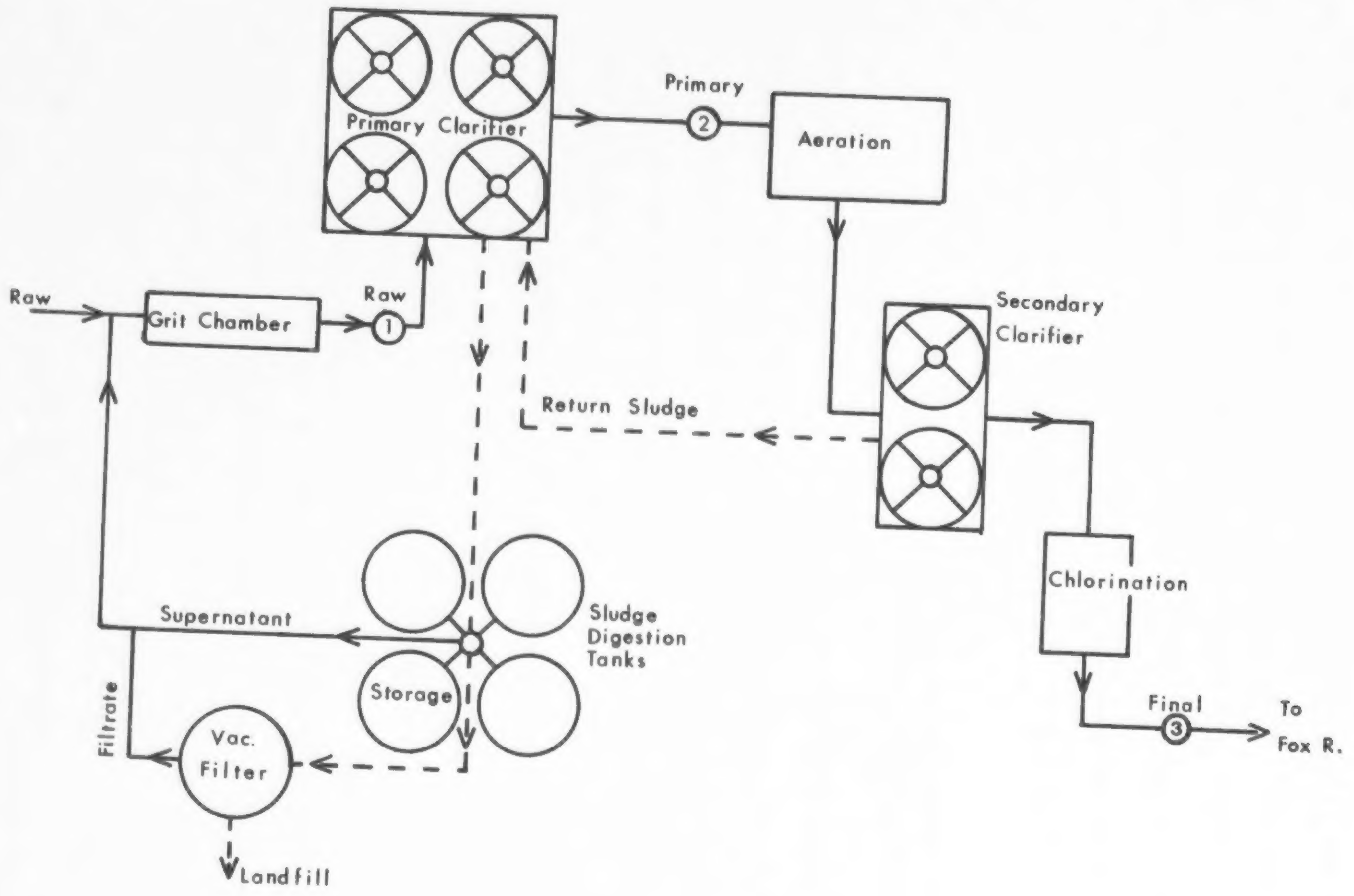
Raw
Grit Chamber
Raw
1
Primary Clarifier
Primary
2
Aeration
Secondary
Clarifier
Return Sludge
Chlorination
Final
3
To
Fox R.
Supernatant
Sludge
Digestion
Tanks
Storage
Filtrate
Vac.
Filter
Landfill

Figure 31. Appleton Sewage Treatment Plant

Kimberly Sewage Treatment Plant
Kimberly, Wisconsin

The Kimberly Sewage Treatment Plant ceased operation when connection with the Heart of the Valley Sewage Treatment Plant was completed. The Kimberly STP was in operation at the time of this study and consisted of preaeration and grit removal, primary clarifier, two aeration basins, two final clarifiers, and chlorination prior to discharge directly to the Fox River. Phosphorus removal was accomplished by addition of liquid alum to the primary clarifier effluent. The plant served a population of about 6,500. One final effluent sample was taken.

Little Chute Sewage Treatment Plant
Village of Little Chute, Wisconsin

The sewage treatment plant consisted of the following units: comminutor, two mechanical sewage lifts, preaeration basin with mechanical aeration and grit removal, two circular activated sludge systems operated in Parshall tank configuration with the contact, reaeration and digestion zones outside, and the clarifier inside. Aerobically digested sludge was pumped to a holding tank prior to disposal. Disinfection occurred in the final clarifier effluent. Liquid alum was added to the clarifier influent for phosphorus removal.

Supernatant from the sludge holding tank was drawn off and rerouted through the plant. When clear supernatant could no longer be drawn, the liquid sludge was hauled by tank truck to a farm field near Little Chute.

This facility is scheduled for dismantling after connection to the Heart of the Valley Sewage Teatment Plant. One final effluent sample was taken.

Heart of the Valley Metro Sewerage District (HVMSD)
(Kaukauna, and Combined Locks)
Kaukauna, Wisconsin

The HVMSD (Kaukauna) Sewage Treatment Plant serves the City of Kaukauna, Kimberly, Little Chute, and the Village of Combined Locks--a total domestic population of about 21,000 and several minor industrial contributors. Only the City of Kaukauna and Village of Combined Locks were serviced by this facility during the investigation.

At the time of the survey the treatment plant consisted of a bar screen, barminutor, two primary clarifiers, three aeration tanks, two final clarifiers, chlorine contact tank, sludge degritter, gravity sludge thickener, two anaerobic sludge digesters, and two sludge lagoons.

About 40 pounds of chlorine were utilized daily for the disinfection of the plant effluent. The chlorine feed rate was manually regulated, based on residual chlorine readings.

The two sludge digesters were operated in series. The digested sludge from the secondary digester was normally hauled by truck to agricultural land for ultimate disposal. The two lagoons were utilized when the liquid sludge could not be hauled.

The final discharge point is located underwater in the Fox River. A total plant bypass is located ahead of the plant and discharges through a separate outfall. This bypass is only utilized in the event of a power outage. Raw and final effluent samples were taken.

Wrightstown Sewage Treatment Plant
Greenleaf, Wisconsin

The Wrightstown Sanitary District operates an extended aeration sewage treatment facility followed by a polishing pond. Raw sewage flows directly to the aeration basin and from there to the clarifier. Effluent from the clarifier is chlorinated prior to entering a polishing/detention pond. Activated sludge is returned to the aeration basin, and waste sludge from the aeration basin and clarifier is pumped to a sludge holding tank when necessary. Supernatant from the sludge holding tank is returned to the system and waste sludge is hauled away.

Effluent from the detention pond flows to a ditch that leads to the East River, which flows several miles before entering the Fox River. This plant would be expected to have only minimal impact on the Lower Fox River or Green Bay. One final effluent sample was taken.

DePere Sewage Treatment Plant
DePere, Wisconsin

The DePere Sewage Treatment Plant serves a population of about 30,000 people. Significant industrial dischargers include Morning Glory Dairy and Armour & Company, located in the town of Ashwaubenon, and U.S. Paper Mills of DePere.

Wastewater treatment consists of degritting and primary clarification followed by conventional activated sludge and final clarification. Clarified effluent is chlorinated prior to discharge to the Fox River. Waste-activated sludge, along with primary sludge, is thickened prior to being further treated in anaerobic digesters. Return activated sludge

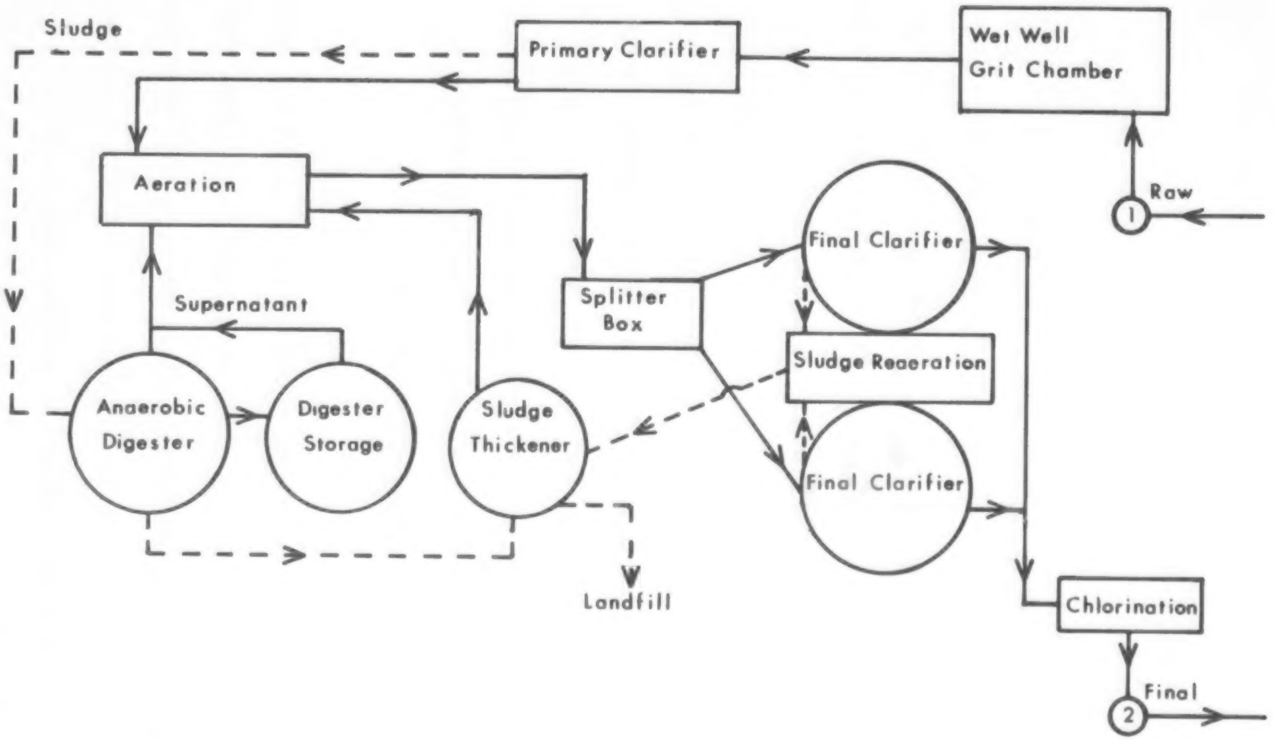
Sludge
Primary Clarifier
Wet Well
Grit Chamber
Aeration
Raw
1
Final Clarifier
Supernatant
Splitter
Box
Sludge Reaeration
Anaerobic
Digester
Digester
Storage
Sludge
Thickener
Final Clarifier
Chlorination
Landfill
Final
2

Figure 32. DePere Sewage Treatment System

is preaerated. Alum is added to the aeration tank effluent for phosphorus removal. A private contractor hauls the digested sludge to a lagoon south of DePere. Figure 32 is a diagram of the plant and sampling locations.

Green Bay Metropolitan Sewerage District (GBMSD)
Green Bay, Wisconsin

Joint treatment of the wastewaters from American Can Company and Proctor & Gamble Paper Products is provided through a tripartite agreement between the GBMSD, the City of Green Bay, and the two industries. Other significant dischargers include the following: Reimer Meat Products; Ultra Plating; Gardner Denver; Chicago & Northwestern Transportation Company; Packerland Packing Company; Green Bay Soap Company; L.D. Schreiber Cheese Company, Incorporated; Green Bay Food Company; Green Bay Canning Company; The Larsen Company; Pauly Cheese Company; Fairmont Foods Company; Food Machine Corporation; Green Bay Drop Forge; Sure Way Supermarkets No.'s 5 & 6; Gold Bond Ice Cream; Diana Manufacturing Company; Fort Howard Steel & Wire Company; Model-Royal Cleaners & Launders; F. Hurlbut Company; Mrs. Karl's Bakery; and Lov-It Creamery, Incorporated.

Wastewater treatment consists of screening and degritting raw metro wastes, followed by primary clarification. Clarified metro wastes are then combined with the paper mill wastes and discharged to aeration tanks for treatment in the contact-stabilization mode of the activated sludge process. Wastewater then flows to final clarifiers and a chlorine contact tank prior to being discharged to the Fox River/Green Bay.

Phosphorous removal is accomplished by the addition of alum to primary clarifier influents.

Solids handling facilities consist of gravity thickeners, dissolved air flotation thickeners, sludge holding tanks, heat treatment (Zimpro wet air oxidation) units, decant tanks, equalization tanks, grease concentrators, vacuum filters, and multiple hearth incinerators. Effluent from these units is returned to the raw sewage wet well, and effluent from the air flotation units is returned to the primary clarifier effluent along with return activated sludge.

Sludge produced in the treatment process is incinerated and the ash is hauled to a landfill site. Figure 33 is a schematic of the treatment facility and indicates sampling locations.

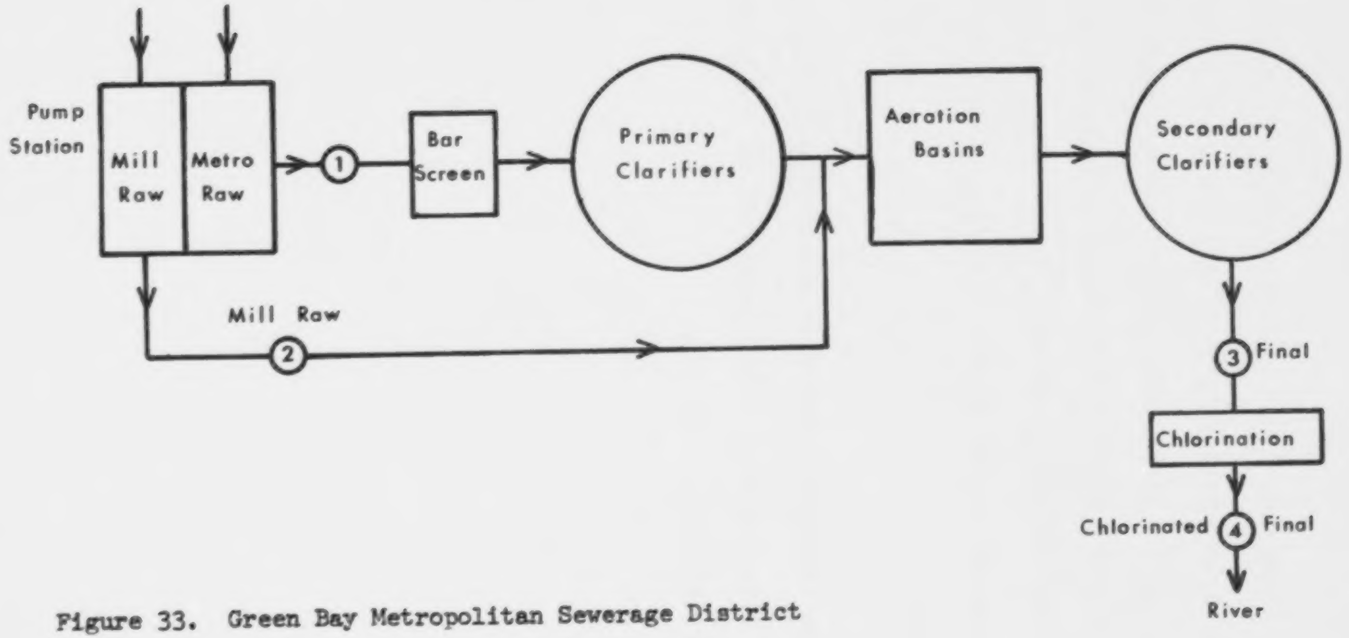
Pump
Station
Mill
Raw
Metro
Raw
1
Bar
Screen
Primary
Clarifiers
Aeration
Basins
Secondary
Clarifiers
Mill Raw
2
3
Final
Chlorination
Chlorinated
4
Final
River

Figure 33. Green Bay Metropolitan Sewerage District

Table 2. Average Flow, BOD and Suspended Solids Discharged to the Fox River.

		Flow	BOD		Suspended Solids	
Discharger	Discharge Period	MGD	mg/L	lbs/day	mg/L	lbs/day
Kimberly-Clark Corp. Badger Globe & Neenah	1977	3.96	7.7	255	13.6	450
Bergstrom Paper Co.	1977	3.723	191.5	8528	304.4	13556
Kimberly-Clark, Lake View	1977	0.903	50	1090	13	317
George Whiting	1977	0.273	88	201	58	143
Wisconsin Tissue	1977	1.711	11.9	170	16.5	235
Riverside Paper	1977	0.734	84	450	138	480
Consolidated Appleton	1977	1.181	1520	14973	88	867
Midtec Paper	1977	7.358	98	7278	135	10082
NCR Appleton Papers	1977	4.497	79	4131	57	2970
Thilmany	1977	22.8	32.5	6192	48.5	9219
Nicolet Paper Co.	1977	2.435	19.1	646	20	675
Fort Howard Paper Company	1977	18.21	29.3	4450	33.4	5080
American Can Company	1977	3.65	18	1016	Not Available	
Proctor & Gamble	1977	5.031	41	1925	76.4	3565
Green Bay Packaging	1977	0.96	45	607	8	102
Neenah-Menasha STP	11/76-09/77	8.77	12.85	940	26.02	1903
Town of Menasha, East	10/76-09/77	0.56	23.78	111	17.92	84
Town of Menasha, West	10/76-09/77	0.55	12.84	59	12.06	55
Butte des Morts Utility District	02/77-09/77	0.74	49.1	303	94.4	583
Appleton STP	10/76-09/77	10.17	67.27	5706	88.25	7485
Kimberly STP	10/76-09/77	0.43	24.16	87	30.16	108

Table 2. Continued

Little Chute STP	10/76-09/77	0.57	33.89	161	15.84	75
Heart of the Valley	02/77-09/77	1.9	9.75	154	12.55	199
Wrightstown STP	11/76-09/77	0.113	83.6	79	61.0	57
DePere STP	10/76-09/77	2.05	71.3	1219	38.5	658
Green Bay Metro Sewerage District	01/77-09/77	10.28	18.23	1563	26.7	2289

VI. RESULTS AND DISCUSSION

PULP/PAPER MILL AND SEWAGE TREATMENT PLANT EFFLUENTS

The results of GC/EC analyses and suspended solids measurements of wastewaters are presented in Table 3. The sampling location within the various facilities is indicated on the treatment system figures described previously in the wastewater treatment facility section. The detection limit for PCBs and pentachloroanisole was 0.2 ug/L and 0.1 ug/L, respectively. The detection limit for the chloro-phenols and chloro-guaiacols depends on GH column conditions and whether and acid fraction was methylated before injection. When the project began, adequate hood space to safely methylate this fraction was not available. Until that time, the acid fraction was directly injected onto the SP-1000 acid-treated column in the GC/EC, resulting in less sensitivity (ca. limit of 10 ug/L for PCP). Another problem with the analysis of chloro-phenols and chloro-guaiacols concerned their degradation in solution in bright light. Their degradation was minimized by methylation.

Polychlorinated biphenyls were detected in the discharge of 12 of the 26 facilities sampled. Arochlor 1242 was the predominant mixture detected. However, other mixtures (Arochlor 1248 and 1254) were occasionally detected,as noted in Table 3. Concentrations of PCBs ranged from the limit of detectability (0.2 ug/L) to 8,200 ug/L in one sample from the grit chamber wet well of Wisconsin Tissue Mill. The data in Table 3 indicate significant PCB concentrations are associated with mills using recycled fiber in their process. The data also indicates that PCBs are associated with suspended solids and efficient solids removal also

Table 3. Pulp and Paper Mill, and Sewage Treatment Plant Effluents - Quantified Results

Pulp and Paper Mills	Date	Sample Source	Sample Type	Suspended Solids (mg/L)	Chloro-organics (ug/L) PCB*	Pentachloro-phenol (PCP)	Pentachloro-anisole (PCA)	Others** by GC
1. Kimberly Clark - Badger Globe, Joint Treatment	11/30/76	Final	grab	-	< 0.2	< 1	0 .07	
	2/28/77	Raw	24 hr. comp.	144	< 0.2	<10	<0 .05	
	2/28/77	Primary	24 hr. comp.	40	< 0.2	<10	0 .12	4CP 2.2
	2/28/77	Final	24 hr. comp.	26	0.3	-	0 .14	
	7/19/77	Final	24 hr. comp.	5	< 0.2	<0.1	0 .05	
2. Bergstrom Paper Company	11/30/76	Final	6 hr. comp.	-	9.5	10		4CG 14, 3CG 12, DHA 3200
	1/26/77	Raw	24 hr. comp.	-	x			
	1/26/77	Final	24 hr. comp.	-	40			
	2/28/77	Raw	24 hr. comp.	2840	79	-	x	
	2/28/77	Final	24 hr. comp.	540	69	<10	x	
	3/02/77	Raw	24 hr. comp.	-	80	1	-	4CG 6
	3/02/77	Primary	24 hr. comp.	-	29	-	x	
	3/02/77	Final	24 hr. comp.	-	56	< 1	-	
	7/18/77	Raw	24 hr. comp.	2580	<10	< 5	<0.1	3CG 10.5
	7/19/77	Final	24 hr. comp.	195	25	<10	x	
	8/09/77	Final	grab	148	16	-	-	
4. Kimberly Clark Lake View	11/30/76	Final	4 hr. comp.	-	0.2	<10	<0.1	
	2/28/77	Final	24 hr. comp.	40	0.15	-	<0.1	
	3/24/77	Raw	24 hr. comp.	660	19.0	<10	-	
	3/24/77	Final	24 hr. comp.	13	1.2	<20	<0.1	
	7/19/77	Final	24 hr. comp.	18	<0.3	<0.1	<0.1	3CP< 0.1
5. George Whiting Paper Co.	11/30/76	Final	4 hr. comp.	-	<0.2		<0.1	
	7/19/77	Raw	grab	48	<0.2	<1.0	0.04	
	7/19/77	Final	24 hr. comp.	46	<0.2	0.35	<0.1	

Table 3. Continued

Pulp and Paper Mills	Date	Sample Source	Sample Type	Suspended Solids (mg/L)	Chloro-organics (ug/L) PCB*	Pentachloro-phenol (PCP)	Pentachloro-anisole (PCA)	Others** by GC
6. Wisconsin Tissue MIll	11/30/76	Final	grab	-	.3	<10	< 0.1	
	2/28/77	Raw	24 hr. comp.	2020	25	-	< 0.1	
	2/28/77	Primary	24 hr. comp.	72	2.2	<10	< 0.1	
	2/28/77	Final	24 hr. comp.	10	1.4	<10	< 0.1	
	7/18/77	Wet Well	grab	21880	8200	-	-	
	7/19/77	Final	24 hr. comp.	5	< .2	< 1	< 0.1	3CP < 0.5
10. Riverside Paper Company	12/02/76	Final	Split Grab	-	< 0.1	<10	< 0.1	
	12/02/76	Final	Split Grab	-	< 0.1	<10	< 0.1	
11. Consolidated Papers, Appleton	12/02/76	Raw	grab	-	< 0.2		0.1	4CP 2.3
	12/02/76	Final	grab	-	7(1254)	x	x	
	7/21/77	Final	24 hr. comp.	79	< 0.2	-	0.07	
	8/10/77	Final	grab	37	-	-	-	3CG 43, DHA 8500
13. Midtec Paper	12/02/76	Final	24 hr. comp.	-	< 0.1	<10	< 0.1	
	3/02/77	Raw	24 hr. comp.	860	< 0.2	<0.1	-	
	3/02/77	Final	24 hr. comp.	38	< 0.2	<10	< 0.1	
	7/20/77	Raw	24 hr. comp.	750	< 0.2	<20	< 0.1	
	7/21/77	Final	24 hr. comp.	23	< 0.3	< 1	< 0.1	
16. Appleton Papers	12/02/76	Final	24 hr. comp.	-	< 0.2	<10	< 0.1	
	3/03/77	Raw	24 hr. comp.	1550	< 0.2	-	< 0.1	
	3/03/77	Primary	24 hr. comp.	62	< 0.2	<20	< 0.1	
	3/03/77	Final	24 hr. comp.	35	< 0.2	-	0.1	
	7/21/77	Raw	grab	936	< 0.2	<10	< 0.1	DHA 69, 3CP 0.8
	7/21/77	Final	grab	98	< 0.2	<20	0.38	
17. Thilmany Pulp and Paper	12/03/76	Final	5 hr. comp.	-	< 0.2	30	< 0.1	
	3/03/77	Raw	grab	580	< 0.2	-	< 0.1	
	3/03/77	Final	2 hr. comp.	68	< 0.2	<10	< 0.1	

Table 3. Continued

					Chloro-organics (ug/L)			
Pulp and Paper Mills	Date	Sample Source	Sample Type	Suspended Solids (mg/L)	PCB*	Pentachlorophenol (PCP)	Pentachloroanisole (PCA)	Others** by GC
	7/21/77	Raw	24 hr. comp.	216	< 0.1	8	< 0.1	3CP 9.0
	7/21/77	Lagoon	24 hr. comp.	168	-	33	-	
	7/21/77	Final	24 hr. comp.	76	< 0.1	18	0.13	
21. Nicolet Paper Company	12/05/76	Final	24 hr. comp.	-	< 0.2	<10	< 0.1	
	3/04/77	Raw	grab	108	< 0.3	<10	< 0.1	
	3/04/77	Final	24 hr. comp.	10	< 0.2	<10	< 0.1	
	3/08/77	Raw	24 hr. comp.	196	.2 (1242 + 54)	<10	< 0.1	
	3/08/77	Final	24 hr. comp.	13	< 0.2	<10	< 0.1	
	7/24/77	Final	24 hr. comp.	21	< 0.2	< 5	< 0.1	
23. Fort Howard Paper Company	12/06/76	Final	grab	-	3.7	<10	< 0.1	
	3/05/77	Final	24 hr. comp.	67	1.2	<10	< 0.1	
	4/15/77	Final	24 hr. comp.	50	2.0	<10	< 0.1	
	4/15/77	Final	24 hr. comp.	76	12	<10	< 0.1	
	7/25/77	Final	24 hr. comp.	50	7.7	12	< 0.1	
	8/09/77	Final	24 hr. comp.	102	5.4	x	-	
24. American Can Co., Green Bay	12/07/76	Final	24 hr. comp.	-	< 0.2	<10	< 0.1	
	1/26/77	Raw	24 hr. comp.	516	< 0.2	<10	< 0.1	
	1/26/77	Final	24 hr. comp.	17	< 0.2	<10	< 0.1	
	3/06/77	Raw	24 hr. comp.	388	< 0.2	<10	< 0.1	
	3/06/77	Final	24 hr. comp.	17	< 0.2	<10	0.1	
	7/26/77	Final	24 hr. comp.	58	< 0.2	<1.0	0.2	
25. Proctor and Gamble Paper Products	12/07/76	Final	24 hr. comp.	-	< 0.2	<10	< 0.1	
	3/06/77	Intake H_2O	24 hr. comp.	4	< 0.2	<1.0	< 0.5	
	3/06/77	Final	24 hr. comp.	116	< 0.2	<10	< 0.1	
	7/26/77	Final	24 hr. comp.	72	< 0.3	<1.0	< 0.1	3CP< 0.5
26. Green Bay Packaging	12/07/76	Eff. to River	24 hr. comp.		< 0.2	<10	< 0.1	
	7/26/77	Eff. to River	grab	44	0.37	<0.3	0.01	4CP< 0.2, 3CP <0.1

le 3. Continued

					Chloro-organics (ug/L)			
Sewage Treatment Plants	Date	Sample Source	Sample Type	Suspended Solids (mg/L)	PCB*	Pentachloro-phenol (PCP)	Pentachloro-anisole (PCA)	Others** by GC
3. Neenah - Menasha STP	11/30/76	Raw	grab	-	6.6	-	< 0.1	
	11/30/76	Final	24 hr. comp.	-	0.1	-	0.16	
	2/28/77	Raw	24 hr. comp.	176	< 0.2	2.3	0.15	
	2/28/77	Final	24 hr. comp.	12	< 0.2	1	0.7	
	3/08/77	Raw	24 hr. comp.	324	1.0 (1248 + 54)	-	0.7	
	3/08/77	Primary	24 hr. comp.	80	0.37	-	0.21	
	3/08/77	Final	24 hr. comp.	9	< 0.2	2.3	0.32	4CP 0.9 3CP 3.6
	7/19/77	Final	24 hr. comp.	18	< 0.2	< 0.2	0.17	
7. Town of Menasha East	12/01/76	Final	24 hr. comp.	-	< 0.1	< 10	< 0.1	
8. Town of Menasha West	12/01/76	Final	24 hr. comp.	-	< 0.1	< 10	< 0.1	
9. Butte des Morts Utility District	12/02/76	Final	24 hr. comp.	-	< 0.2	< 0.1	< 0.1	
	12/02/76	Final	grab	-	< 0.2	< 10	-	
12. Appleton STP	12/02/76	Raw	grab	-	23	-	-	
	12/02/76	Final	24 hr. comp.	-	< 0.2	< 2.0	< 0.1	3CP 5.4
	3/02/77	Raw	24 hr. comp.	448	1.4	< 20	< 0.1	
	3/02/77	Primary	24 hr. comp.	136	0.4	< 10	< 0.1	
	3/02/77	Final	24 hr. comp.	40	0.6	< 10	< 0.1	
	7/21/77	Raw	24 hr. comp.	340	1.3	9	< 0.1	3CP 13
	7/21/77	Final	24 hr. comp.	78	< 0.2	< 10	< 0.1	3CP 5
14. Kimberly STP	12/02/77	Final	24 hr. comp.	-	< 0.2	< 0.1	< 0.1	3CG, 3CP < 0.1
15. Little Chute STP	12/02/76	Final	grab	-	< 0.2	< 5.0	< 0.1	
18. Heart of the Valley STP	12/03/76	Final	grab	-	< 0.2	< 10	< 0.1	
	3/03/77	Raw	24 hr. comp.	86	< 0.2	< 1.0	< 0.1	3CP, 4CG < 0.5
	3/03/77	Final	24 hr. comp.	46	< 0.2	< 10	< 0.1	
	7/21/77	Final	grab	6	< 0.2	0.25	< 0.1	

Table 3. Continued

Sewage Treatment Plants	Date	Sample Source	Sample Type	Suspended Solids (mg/L)	Chloro-organics (ug/L)			
					PCB*	Pentachloro-phenol (PCP)	Pentachloro-anisole (PCA)	Others** by GC
20. Wrightstown STP	12/03/76	Final	24 hr. comp.		0.36(1254)	-	0.07	
22. DePere STP	12/05/76	Final	grab	-	< 0.2	< 10	< 0.1	
	3/04/77	Raw	24 hr. comp.	260	0.5	-		
	3/04/77	Final	24 hr. comp.	35	0.6	< 1.0	< 0.1	
	7/24/77	Final	24 hr. comp.	12	< 0.2	17	< 0.1	
27. Green Bay STP	12/08/76	Final	grab	-	< 0.2	-	0.9	
	3/06/77	Combined Raw	24 hr. comp.	116	< 0.2	-	< 0.9	
	3/06/77	Final w/o Cl_2	24 hr. comp.	25	< 0.2	< 10	0.03	TCA 0.08/4CG,3CP < 10
	3/06/77	Final w Cl_2	24 hr. comp.	24	< 0.2	< 10	< 0.1	TCA 0.04
	7/26/77	Combined Raw	24 hr. comp.	184	< 0.3	0.08	-	
	7/26/77	Mill Raw	24 hr. comp.	180	< 0.3	< 5.0	< 0.1	
	7/26/77	Metro Raw	24 hr. comp	216	< 0.2	2.7	< 0.1	
	7/26/77	Final	24 hr. comp	60	< 0.3	0.7	0.04	

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* Appear to be Aroclor 1242 except where indicated

** 4CP = Tetrachlorophenol, 4CG = Tetrachloroguaiacol, 3CG = Trichloroguaiacol, 3CP = Trichlorophenol, DHA = Dehydroabietic Acid,TCA = Trichloroanisole

A blank space indicates that none was detected.

- Indicates not run

removes PCBs from the final effluent. Other studies have also linked PCBs with particulates in water and wastewater (69, 83). Wisconsin Tissue Mill operates an efficient waste treatment system as indicated by analyses of its wastewater samples. Samples collected on February 28, 1977 show both suspended solids (2020 mg/L) and PCBs (25 ug/L) were high in the raw wastewater. However, the primary clarifier and final effluent samples show a dramatic decrease. In the final effluent, the PCB concentration was reduced from 25 to 1.4 ug/L while suspended solids were reduced from 2020 to 10 mg/L. Similar relationships are shown by the sample analyses from Kimberly-Clark Lake View and the Neenah-Menasha and Appleton Sewage Treatment Plants. Samples collected on November 30, 1976 from the Neenah-Menasha STP were not analyzed for suspended solids, but PCBs were reduced from 6.6 ug/L in raw to 0.1 ug/L in final effluent. Samples collected from the same facility on March 8, 1977 show a reduction in suspended solids from 324 to 80 mg/L and a corresponding reduction in PCBs from 1.0 to .37 ug/L. The Appleton STP samples show PCB raw to final effluent reductions from 23 to < 0.2, 1.4 to .6, and 1.3 to <0.2 ug/L with corresponding suspended solids reductions.

Similar reductions for other chloro-organic compounds may also occur and include the following compounds identified by GC analysis: tetrachlorophenol, trichlorophenol, tetrachloroguaiacol, trichloroguaiacol and dehydroabietic acid. **This relationship needs further study.**

Most of the PCBs entering a sewage treatment plant becomes dissolved in or absorbed on the suspended particulate matter and are removed with the sludge during the primary and secondary stages of treatment (99, 69, 65). The same relationship has been considered valid for PCBs in wastewater from paper mills using recycled paper fibers as a raw material (88). Recent work on effluents from pulping and bleaching mills indicates effective removal of many organic toxicants by most of the waste treatment systems under investigation (59). However, very little removal of fatty acids, resin acids, or bleach toxicants occurred during primary clarification, which suggests that these compounds were not associated with the suspended solids removed.

Table 4 presents data on wastewater effluents extracted from Table 3. The data are presented to show relationships among suspended solids, PCB concentration, and stage of waste treatment at selected paper mills and sewage treatment plants.

Table 4. Relationship between PCB concentration and suspended solids in paper mills and sewage treatment plants.

Mill	Date	Sample Source	Suspended Solids (mg/L)	PCB (mg/L)
Bergstrom Paper Co.	2/28/77	Raw	2840	79
	2/28/77	Final	540	68
Kimberly-Clark-Lakeview	3/24/77	Raw	660	19
	3/24/77	Final	13	1.2
Wisconsin Tissue Mill	2/28/77	Raw	2020	25
	2/28/77	Primary	72	2.2
	2/28/77	Final	10	1.4
Neenah Menasha STP	3/08/77	Raw	324	1.0
	3/08/77	Primary	80	0.37
	3/08/77	Final	9	<0.2
Appleton STP	3/02/77	Raw	448	1.4
	3/02/77	Primary	136	0.4

Table 4. Continued

Mill	Date	Sample Source	Suspended Solids (mg/L)	PCB (mg/L)
DePere STP	3/02/77	Final	40	0.6
	7/21/77	Raw	340	1.3
	7/21/77	Final	78	0.2
	3/04/78	Raw	260	0.5
	3/04/78	Final	35	0.6

In general, there is a decrease in PCB concentration with advanced treatment and suspended solids removal. It should be noted that Bergstrom Paper Company has nearly the same waste treatment system as Wisconsin Tissue Mill. However, Bergstrom's treatment system does not appear to be efficient in removing solids or PCBs. This may be a function of loading or waste character. Further investigation of this situation is necessary.

Some laboratory measurements were made on final effluents to demonstrate that additional solids removal could reduce PCB levels beyond what is currently being achieved.

Table 5 presents the results of a test to measure the effect of filtration of Fort Howard's final effluent PCB concentration. By passing the waste water through a Reeve Angel (Grade 202) filter, 54 percent of the PCBs were removed. This reduction may be partly due to absorption to the filter as well as to removing particles that have PCBs associated with them.

Table 5. Effect of Filtration on PCB Concentration in Final Effluent from Fort Howard Paper Company.*

Test	PCB Concentration (ug/L)
Unfiltered	7.7
Filtered	4.2

Reduction = 46%

* Filtration through a Reeve Angel Grade 202 filter.

Table 6 shows results of measurements on the effect of centrifuging selected final effluents. Centrifugation was effective in removing 46 percent of the PCB content in final effluent from Fort Howard Paper Company and the Bergstrom Paper Company. The same treatment was able to remove 29 percent of the trichloroguaiacol present in the final effluent of the Consolidated Paper Company,even though the solids were already low.

Table 6. Effect of Centrifugation on Selected Chloro-organics in Final Effluents.

Mill	Suspended Solids Before Centrifugation (mg/L)	Concentration (ug/L) Before	After	% Removal
		PCB		
Fort Howard Paper Company	102	5.4	2.9	46
Bergstrom Paper Company	148	16.0	8.7	46
		Trichloroguaiacol		
Consolidated Paper Company	37	43	35	29

The data suggest that additional waste treatment could be effective in removing PCBs and perhaps other chloro-organics from waste waters.

The significant concentrations of pentachlorophenol found in some of the Thilmany Pulp and Paper Company wastewaters were traced to the use of "Nalco 201." Nalco 201 contains 16 percent pentachlorophenate and 8 percent trichlorophenate. This product was being used in an alum truck to control slimes. It was also found that "Nalco 76-31," which contains chlorophenate, was being used as a slimicide in recycled trim (broke) paper. The mill has indicated these compounds are no longer used.

Other compounds detected and quantified by GC/EC in Table 3 were usually accomplished only after their identification by GC/MS and when standards were available. A complete tabulation of compounds identified, and unidentified compounds characterized by GC/MS, is presented in the Appendices.

More than 100 compounds identified by GC/MS are listed in Table 7. Appendix A also lists the compounds, along with their source, location, and extract of the sample(s) containing them. The data in Appendix A show how each mass spectrum was identified, along with pertinent literature references. The compounds are listed as they were detected, except for those identified as methylated derivatives. Other compounds, which were characterized but remain unidentifed, are listed in Appendix B.

To assess the significance of the compounds detected in this study, certain categories were assigned. Twenty compounds in Table 7 appear in the EPA consent decree (CD) Priority Pollutant List (20). These include some nonchlorinated compounds that are not detected efficiently by

Table 7. Chlorinated and Nonchlorinated Organic Compounds Identified in Samples from the Lower Fox River Watershed.

---

*Acenapthene
Acetone, Tetrachloro-
Acetovanillone
Aniline, Trichloro-
Anisole, Pentachloro-
*Anthracene (or Phenanthrene)
Bezene, Dichloro-diethyl-
Benzoate, Dimethyl-
Benzoate, Methyl-methoxy-
Benzoic acid
Benzoic acid, Isopropyl-
Benzophenanthrene, Methyl-
  or (Benzanthracene, Methyl-)
Benzophenone
Benzothiazole
Benzothiazole, Hydroxy-
Benzothiazole, Methyl-thio-
Benzyl alcohol
Biphenyl
Biphenyl, Methyl-
Bisphenol A
Bisphenol A, Chloro-
Bisphenol A, Dichloro- (2 isomers)
Bisphenol A, Tetrachloro-
Bisphenol A, Trichloro-
Borneol, Iso-
Caffeine
Camphor, Oxo-
Carbazole
*Chlordane
*Chrysene
*DDD
*DDE
*DDT
Dodecane

FATTY ACIDS

Heptadecanoic Acid
Lauric Acid
Myristic Acid
Oleic Acid
Palmitic Acid
Stearic Acid

FATTY ACIDS, METHYL ESTERS

Methyl palmitate
Methyl stearate
*Fluoranthene
Guaiaol
Guaiacol, Dichoro-(3 isomers)
Guaiacol, Tetrachloro-
Guaiacol, Trichloro- (3 isomers)
Heptadecane
*Hexachlorocyclohexane (Lindane)
*Hexachlorocyclopentadiene
Hexadecane
Indole, Chloro-p- Menth-4-ene-3-one
Naphthalene, Isopropyl-
Naphthalene, Methyl-
Nonadecane
Octadecane
Pentadecane
Phenanthrene, Methyl-

*Phenanthrene, Methyl-
*Phenol
Phenol, p-Tertiary Amyl-
*Phenol, Chloro-
Phenol, p-(α-chloroethyl)-
Phenol, Decyl-
*Phenol, Dichloro- (2 isomers)
Phenol, Ethyl-
Phenol, Nonyl- (3 isomers)
*Phenol, Pentachloro-
Phenol, Tetrachloro-
  (2,3,4,6 or 2,3,5,6)
Phenol, Trichloro-
* (2,4,6)
  (2,4,5 or 2,3,4)
Phenol, Trichloro-dimethoxy-
Phenol, Undecyl-
Phenyl, Decane
Phenyl Dodecane
Phenyl Undecane
Phosphate, Tributyl-

PHTHALATES

*Dibutyl Phthalate
*Diethyl Phthalate
*Dioctyl Phthalate

*Polychlorinated Biphenyls (PCBs)
Propan-2-one, 1-(4-hydroxy-3-methoxy
  phenyl) or guaiacyl acetone
*Pyrene

RESIN ACIDS

6,8,11,13 Abietatetraen-18-oic Acid
Dehydroabietic Acid
Oxo-dehydroabietic Acid
Pimaric Acid
Sandaracopimaric Acid

RESIN ACIDS, METHYL ESTERS

Methyl Dehydroabietate

RESIN ACIDS, CHLORINATED

Chlorodehydroabietic Acid (2 isomers)
Dichlorodehydroabietic Acid

RESIN ACID METHYL ESTERS, CHLORINATED

Methyl Chlorodehydroabietate
Methyl Dichlorodehydroabietate

Salicylic Acid
Syringaldehyde
Syringaldehyde, Chloro-
Tetradecane
Toluene, Dichloro-
Vanillin
Vanillic Acid
Veratrole, Dichloro-
Veratrole, Trichloro-
Xylene, Dichloro-
Xylene, Trichloro-

---

*Compounds found on EPA Consent Decree Priority Pollutant List (20).

GC/EC. Other compounds observed in pulp and paper mill wastes match those found to be toxic to fish by other investigators, including Fox et al. (21), Leach and Thakore (22-28), Lockhart and Leach (29), McKague et al. (30), Rogers and Keith (31), and Walden (32). Compounds prefixed with P/T (toxics from paper mill wastes) in Appendix A include chloroguaiacols, resin acids, chloro-resin acids, and oleic acid. Many other compounds previously reported in paper mill wastes were also found in this study and are designated by the prefix P. These include acetovanillone, fatty acids, guaiacol, guaiacyl acetone, methyl thiobenzothiazole, syringaldehyde, vanillin, and vanillic acid. Of the remaining compounds in Appendix A, six are polycyclic aromatic hydrocarbons (PAHs). Two compounds commonly used in industry, i.e. nonyl phenol (present in surfactants) and benzothiazole (an antioxidant), appear in Appendix A. Alkanes, such as hexadecane, have been used in kerosene-based defoamers (Webb et al. (33)). Bisphenol A could have been used as a fungicide (89).

Some compounds found in final effluents were quantitated by GC/FID (flame ionization detector) and/or GC/MS. Various effluents and extraction efficiencies were experienced; therefore only concentration ranges (in ug/L) are given here: benzothiazole (10-30), hydroxybenzothiazole (10-30), methyl thiobenzothiazole (10-40), trichloroguaiacols (10-60), tetrachlorophenol (2-20), pentachlorophenol (5-40), dehydroabietic acid (100-8500), and PAHs (0.5-10). The concentrations of these generally corroborate earlier investigations by Rogers (90), Rogers and Keith (31) Keith (45), Brownlee and Strachan (34), and others noted in Appendix A.

Although a few samples contained chloro-guaiacols, many contained various isomers of the mono to penta chloro-phenols as well as PCBs. The source of chloro-phenols in mill wastewaters has not yet been determined. Chloro-phenols could have been used by paper mills for slime control. Since chloro-guiacols were not found in some mill wastewaters, this may indicate that these mills do not bleach their pulp or that they purchase pulp and/or de-ink recycled paper. Bergstrom Paper Company, Mill 2, which acquires its pulp equally through purchase and de-inking, is one major exception. Its wastewater contained not only chloro-guaiacols and chloro-phenols but also relatively large amounts of resin acids, especially dehydroabietic acid (up to 3.2 mg/L). This resin acid appears to be the most stable of the resin acids, as shown by Brownlee and Strachan (34) and Fox et al. (35). The toxicity of resin acids to fish has been known since 1936. The lethal threshold concentration of dehydroabietic acid for young sockeye salmon was found to be 2 mg/L by Rogers (90). Leach and Thakore (28) reported a 96 hr. LC 50 of 0.75 mg/L for dehydroabietic acid using coho salmon. The resin acids and fatty acids from this mill could have come from the use of rosin or tall oil (89). Our observations of chloro-phenols corroborate work by Lindstrom et al. (36). However, we did not detect any chloro-catechols. Whenever chloro-vertrole derivatives were detected in methylated acidic fractions, chloro-guaiacols had been detected in these acidic fractions before methylation.

Given the sampling locations, it is very difficult to determine which chloro-organic compound found in a particular mill was added during production, formed in the mill, or formed during wastewater treatment. It is possible, but yet unproven, that chloro-guaiacols, chloro-resin acids, chlorosyringaldehyde, chloro-toluenes, chloro-xylenes, chloroindole, some chloro-phenols and, tentatively, some chloro-bisphenol A's were formed at some point in the mill by reaction with chlorine. It is possible that some of the unidentified compounds listed in Appendix B could have been chlorinated in the paper-making process.

SURFACE WATER AND SESTON

Surface Water

Fox River surface water samples were collected at the 25 stations shown on Figure 34. Sampling was concentrated near Green Bay, Appleton, and Neenah-Menasha because of the presence of most paper mills and sewage treatment plants in these areas. The results of chloro-organic analyses are presented in Table 8 in downstream order.

The low concentrations found in surface water were expected because of the low solubility of chlorobiphenyls in water. Some values for PCB solubility are shown in Table 9. Although there is some disagreement regarding the solubility of PCBs in water, it is generally agreed the solubilities are low and tend to decrease with increasing chlorine content. If PCB concentrations greater than the theoretical solubility in water were found, it would most likely be due to PCBs associated with suspended solids.

It is difficult to draw any conclusions from the data in Table 8 since most samples did not have chloro-organic concentrations above the analytical detection level. However, some general comments can be made to explain the concentrations found:

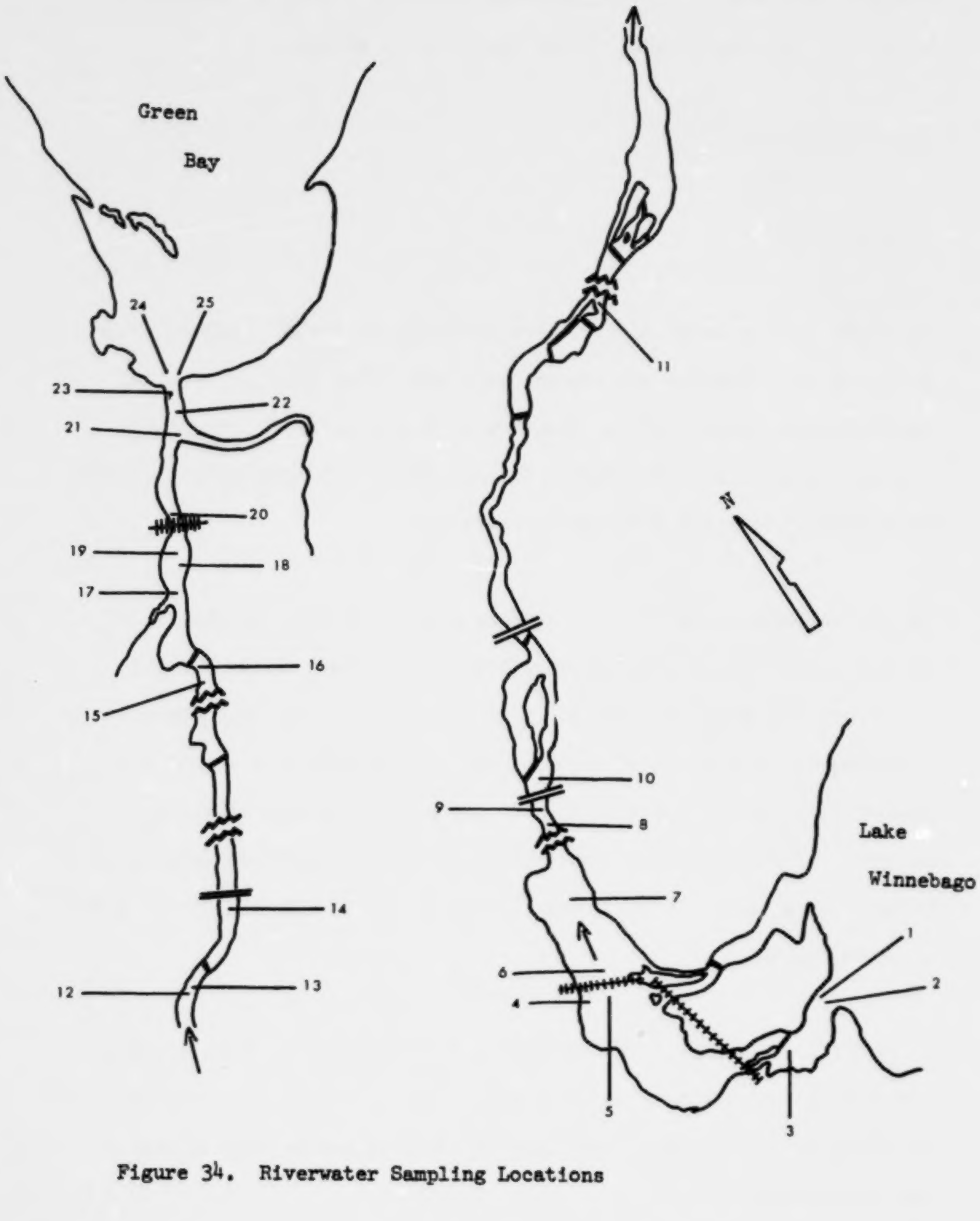
Green
Bay
24
25
23
22
21
20
19
18
17
16
15
14
12
13
11
N
10
9
8
Lake
Winnebago
7
1
6
2
4
5
3

Figure 34. Riverwater Sampling Locations

Table 8. Concentration of Chloro-organics (ug/L) Found in Unfiltered Fox River Water in Downstream Order.

Sample Number	Date	PCB	Other Chloro-organics**				
			3CP	4CP	PCP	PCA	DDE
1	2/27/77	<0.1					
2*	7/19/77	<0.05	<0.5		<0.8	<0.01	
3	11/30/76	<0.1			<0.2	<0.1	
4	2/27/77	0.85			<0.5	<0.1	
5	2/27/77	<0.1			<0.1	<0.05	
6	11/30/76	<0.1					
7	2/27/77	<0.2	<0.05	<0.05	<0.1	<0.05	
8	7/20/77	Lost					
9	3/02/77	0.3				<0.01	
10	2/02/76	<0.1					
11	3/02/77	<0.2				<0.01	
12	3/03/77	<0.2					
13	12/03/76	<0.1					
14*	7/23/77	0.24			<0.5	<0.02	
15	3/03/77	<0.2					
16*	7/25/77	0.14	<0.5	<0.5	<0.5	0.01	
17	3/04/77	<0.2				<0.01	
18	12/06/76	0.12				<0.05	0.004
19*	7/25/77	0.30				<0.02	
20	3/04/77	0.17					
21	3/05/77	<0.2					
22	3/05/77	<0.2	<0.1		<0.1		
23	3/05/77	<0.2			<0.2	<0.05	
24	3/05/77	0.1			<1.0		
25	12/08/76	0.25			<1.0	0.1	

* Seston was collected at these locations at the same time for comparison.

**3CP = Trichlorophenol

4CP = Tetrachlorophenol

PCP = Pentachlorophenol

PCA = Pentachloroanisole

Table 9. Solubility of Chlorobiphenyls in Water*

Compound	Solubility (ppm) (Wollnofer *et al*., 1973)	(Haque and Schmedding, 1975)
Monochlorobiphenyls		
2-	5.9	
3-	3.5	
4-	1.19	
Dichlorobiphenyls		
2,4-	1.40	
2,4'-	1.50	
2,4'-	1.88	0.673 ± 0.004
4,4'-	0.08	
Trichlorobiphenyls		
2,4,4'-	0.085	
2',3,4-	0.078	
2,2',5-	--	0.248 ± 0.004
Tetrachlorobiphenyls		
2,2',5,5'-	0.046	0.0265 ± 0.008
2,2',3,3'-	0.034	
2,2',3,5'-	0.170	
2,2',4,4'-	0.068	
2,3',4,4'-	0.058	
2,3',4',5-	0.041	
3,3',4,4'-	0.175	
Pentachlorobiphenyls		
2,2',3,4,5'-	0.022	
2,2',4,5,5'-	0.031	
Hexachlorobiphenyl		
2,2',4,4',5,5'	0.0088	0.000953 ± 0.00001
Octachlorobiphenyl		
2,2',3,3',4,4',5,5'-	0.0070	
Decachlorobiphenyl	0.015	

* Adapted from Kornreich, M. et. al., 1976 (92)

(1) The Fox River is not saturated with PCBs unless only the very highly chlorinated isomers are present. The presence of only highly chlorinated PCBs is unlikely because most commercial mixtures contain a variety of isomers, from monochloro to at least heptachlorobiphenyl. The PCB mixture most frequently identified was Aroclor 1242, having been found in approximately 90 percent of the samples. Aroclor 1242 is composed mainly of tetrachlorobiphenyl and lesser chlorinated isomers (92). Aroclor 1248 and 1245 were only found occasionally.

(2) Although all surface water concentrations were low, it should be noted that the highest concentrations were found in areas affected by dischargers using recycled paper fibers and other sources discharging PCBs. Thus it appears that higher water concentrations of PCBs are localized and are related to nearby point sources. This finding was expected from information provided by a previous report (88).

Seston

For the purposes of this investigation, seston is defined as the whole heterogenous mixture of living and nonliving substances captured by filtering water through a #20 (80 um) mesh net. PCB residues have been found in plankton sieved through a 106 um net (91). It was recognized that temporal and spatial variations in plankton species composition and particle size affect net-capturing efficiency. Many species of plankton, especially diatoms, can pass through an 80 um net. However, most chloro-organic compounds are believed to be associated with effluent suspended solids and may not be available to living seston in high concentrations. Because the samples represented a fraction of the river's particulate load, unfiltered water samples were collected at four locations for comparison.

The results of chloro-organic measurements on seston samples collected in downstream order are presented in Table 10. Sample site locations are designated on Figure 35. The PCB concentrations are for the volume of water filtered and are thus directly comparable with river water concentrations. The lower detectable levels of PCBs in the seston samples are due to the large volume of water filtered (190-3800 liters). The samples were not analyzed on a dry weight basis because of the possibility of compound loss during the drying process.

Immediately apparent from Table 10 are the low concentrations of PCBs associated with seston in the bulk water. The significance of these levels compared to river water is addressed later in this section. Also apparent is that, as the river water travels downstream, the PCB concentration in seston increases. The increase is steady, from values below detection limits in the Neenah Channel (0.002 ug/L) to 0.029 ug/L at the river mouth. This suggests seston is accumulating PCB throughout the length of the river. The data also suggest PCBs in seston are related to suspended solids discharged in effluents, since effluents are the major chloro-organic source. Thus, effluent suspended solids are likely to make up a significant portion of the river suspended solids. A previous study of seston in the Fox River (11) indicated waste paper fibers discharged to the river tended to settle out a short distance below outfalls. High PCB concentrations in sediments support the theory that PCBs and other chloro-organics are carried to the river bottom with particulate matter. This is one reason why river seston does not contain high PCB concentrations.

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Table 10. Chloro-organic Concentrations (ug/L) Associated with Fox River *Seston*.

Sample #	Date	Water Volume Filtered (liters)	PCB	Pentachloroanisole
1*	7/19/77	190	0.002	0.05
2	7/19/77	380	0.006	
3	7/19/77	190	0.003	0.02
4	11/23/76	3800	0.13	
5	7/20/77	190	0.015	
6	7/21/77	190	0.006	0.045
7	7/22/77	190	0.024	
8	7/22/77	190	Lost	
9*	7/23/77	190	0.025	
10*	7/25/77	190	0.020	
11*	7/25/77	190	0.030	0.05
12	7/26/77	190	0.013	0.1
13	7/26/77	190	0.024	0.05
14	7/26/77	190	0.018	
15	11/23/76	1900	0.020	
16	7/26/77	190	0.029	
			$\bar{x}$ = 0.016	

Seston and Surface Water Relationship

On four occasions, unfiltered riverwater was sampled at the same time and location as seston. Thus the PCBs associated with a size fraction of seston in the water column was investigated. The results of these measurements are shown in Table 11.

The data indicates that about 11 percent of the PCB concentration was associated with the seston. Although only three locations were described, it appears this ratio was relatively consistent. Since the amount of PCB in unfiltered water was always much greater than the amount associated with seston, some observations can be made:

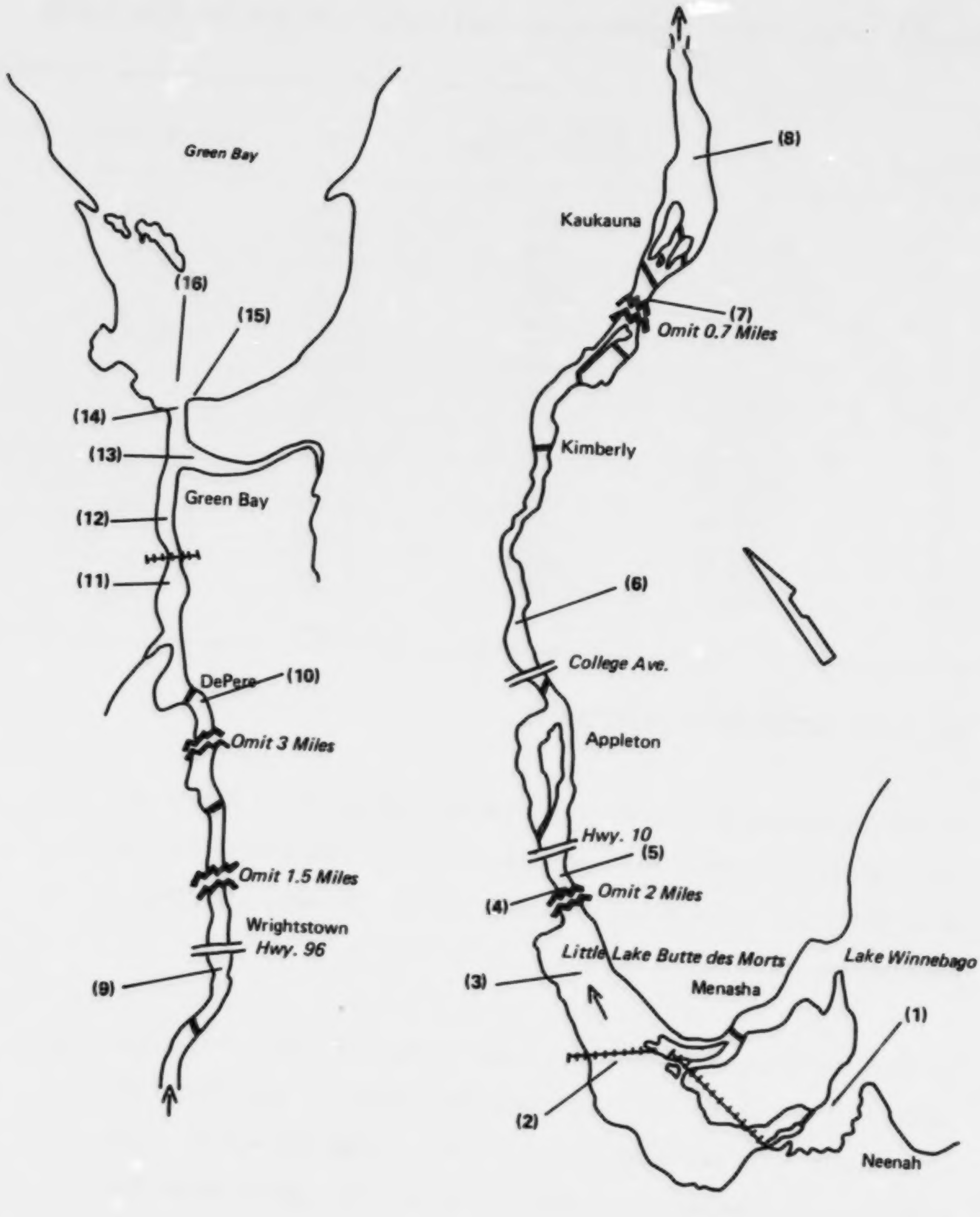
Green Bay
(16)
(15)
(14)
(13)
Green Bay
(12)
(11)
DePere
(10)
Omit 3 Miles
Omit 1.5 Miles
Wrightstown
Hwy. 96
(9)
(8)
Kaukauna
(7)
Omit 0.7 Miles
Kimberly
(6)
College Ave.
Appleton
Hwy. 10
(5)
(4)
Omit 2 Miles
Little Lake Butte des Morts
Lake Winnebago
(3)
Menasha
(1)
(2)
Neenah

Figure 35. Seston Sampling Locations

(1) The PCBs in the water column must be either dissolved or attached to particulates smaller than 80 um. The PCBs' hydrophobic nature should cause them to cluster together or around organic impurities such as oil-like droplets. Thus they would have been sampled as dissolved material. Further study will be required to determine if PCBs are associated with particules less than 80 um.

(2) Once PCBs enter the river system, they can either settle out or float to the water surface. The accumulation of PCBs in sediment is evidenced by the high concentrations found there. However, similar to hydrophobic/lipophilic chlorinated hydrocarbon pesticides, PCBs and their commercial mixtures can be enriched on the surface of water in the lipid phases of a surface organic microlayer (93).

Table 11. PCB Concentration in River Water and Seston

Sample Number		PCB ug/L		% PCB Associated with Seston
Riverwater	Seston	Riverwater	Seston	
2	1	0.05	0.002	N.A.
14	9	0.24	0.025	10
16	10	0.14	0.020	14
19	11	0.30	0.030	10
				$\bar{X}$ = 11

This exposes them to both vaporization into the atmosphere and destructive ultraviolet radiation from the sun. The absence of PCBs from most water samples is probably due to a combination of these effects.

When suspended solids from an effluent containing PCBs are dense enough to settle out of the water column, they will become part of the bottom sediment. However, a fraction of the PCB-contaminated discharge will remain suspended and become part of the river's seston load. Thus, as water travels down the Lower Fox River, the concentration of PCB-contaminated seston becomes greater with an increase in the number of discharge points it passes.

SEDIMENT

Sediment samples for PCB analysis were collected at the 34 stations indicated on Figure 36, and results of the analysis are found in Table 12. Station 1 was established in the Menasha Channel above any known point sources and the PCB concentration was less than 0.05 mg/kg. Nine of the remaining 33 samples were found to contain less than 1 mg/kg, and 24 samples contained PCB concentrations ranging from 1.2 to 61.0 mg/kg on a dry weight basis.

Analysis of sediments from proposed dredging projects during the past few years suggested that PCB concentrations greater than 1 mg/kg are associated with localized point sources (12). Guidelines established by EPA (12) classify sediments containing PCB concentrations of 10 mg/kg or higher as polluted and unacceptable for open lake disposal. The pollution classification of sediments with PCB concentrations between 1.0 and 10.0 mg/kg are to be considered on a case-by-case basis. The Wisconsin DNR considers sediments containing 1 mg/kg or more as a potential hazard and has tentatively established the following guidelines concerning dredge spoil disposal:

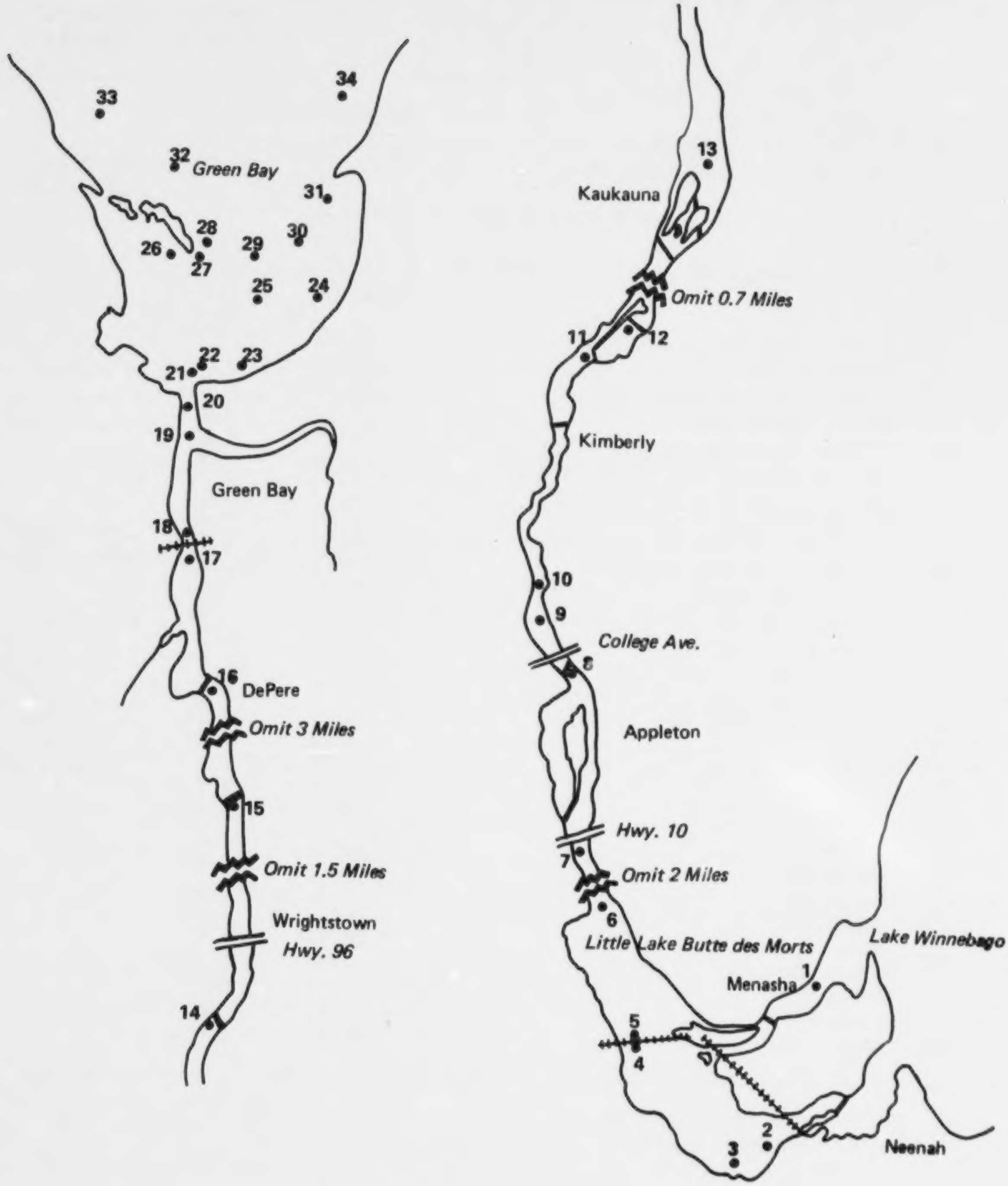
33
34
32
Green Bay
31
28
30
26
29
27
25
24
22
23
21
20
19
Green Bay
18
17
16
DePere
Omit 3 Miles
15
Omit 1.5 Miles
Wrightstown
Hwy. 96
14
13
Kaukauna
Omit 0.7 Miles
11
12
Kimberly
10
9
College Ave.
8
Appleton
Hwy. 10
7
Omit 2 Miles
6
Little Lake Butte des Morts
Lake Winnebago
1
Menasha
5
4
2
3
Neenah

Figure 36. Sediment Sampling Locations

Table 12. PCB Concentrations in Sediment

Station No. and Location	Collection Late	PCB (mg/kg) (dry weight)	Other Compounds* (mg/kg)
1. Menasha Channel	5/23/77	<0.05	
2. Directly below Bergstrom	5/23/77	1.4	
3. 300 yards below Bergstrom	5/23/77	61.0	DHA = 2.7 PCP = 0.22
4. Little Lake Rutte des Morts CNWRR Bridge	5/23/77	1.3	
5. Little Lake Butte des Morts CNWRR Bridge	11/24/76	5.5	
6. Little Lake Butte des Morts Outlet	5/23/77	21.0	
7. Appleton Yacht Club	11/24/76	8.2	
8. Above lower Appleton Dam	5/23/77	9.0	
9. Below Consolidated	5/23/77	1.2	
10. 1 Mile below Consolidated	6/22/77	3.6	
11. Above Kimberly Dam below Midtec	5/23/77	0.9	
12. Above lower Little Chute Dam	5/23/77	5.1	
13. Below Thilmany Paper	6/04/77	4.8	
14. Above Rapide Croche Dam	6/04/77	5.8	PCP = 0.22
15. Above Little Rapids Dam	6/04/77	5.0	PCP = 0.28
16. Above DePere Dam	6/22/77	0.18	
17. Across from Ft. Howard Outfall	5/23/77	0.96	
18. Below Ft. Howard, CNWRR bridge	5/23/77	18.3	
19. Near Mouth of East River	5/24/77	13.0	
20. Above Green Bay STP Near Mouth	5/24/77	2.1	
21. Below Green Bay STP Outfall	11/24/76	38.0	
22. Green Bay	5/24/77	7.5	
23. Green Bay	5/24/77	7.2	
24. Green Bay	5/24/77	4.7	
25. Green Bay	5/24/77	0.12	
26. Green Bay	5/24/77	1.8	
27. Green Bay	5/24/77	0.46	
28. Green Bay	5/24/77	5.6	
29. Green Bay	5/24/77	< 0.05	
30. Green Bay	5/24/77	11.0	
31. Green Bay	5/24/77	2.6	
32. Green Bay	5/24/77	< 0.05	
33. Green Bay	5/24/77	0.02	
34. Green Bay	5/24/77	0.075	

* DHA = Dehydroabietic Acid
PCP = Pentachlorophenol

1 mg/kg	(dry weight)	no restrictions
1-10 mg/kg	(dry weight)	spoil must be disposed of in a contained area
10 mg/kg	(dry weight)	use of silt screen required; spoil must be disposed of in a clay-sealed disposal area or in a licensed toxic and hazardous waste disposal area.

Table 13 is a list of areas polluted with PCBs, according to EPA guidelines.

Table 13. Location of Sediment with PCB Concentration Greater than 10 mg/kg.

Station No.	Location	PCB (mg/kg)
3	300 yards below Bergstrom	61.0
6	Little Lake Butte des Morts outlet	21.0
18	CNWRR bridge below Ft. Howard	18.3
19	Near mouth of East River	13.0
21	Below Green Bay STP outfall	38.0
30	Green Bay near Sable Pt.	11.0

Station 8, above the lower Appleton Dam contained 9 mg/kg. Other stations located in the prevailing eastward current between the mouth of the Fox River and Sable Point in Green Bay contained 2.6 to 7.5 mg/kg of PCBs.

The data indicate the sediments of most of the Lower Fox River and the east side of Green Bay to Sable Point are polluted with significant concentrations of PCBs. It should be noted the highest concentrations were found in silt deposition areas downstream from PCB containing discharges. Station 30 in Green Bay was located near a bar extending from Sable Point, which is probably a silt deposition area.

The sediment samples were collected from the top 6 inches of sediment in all cases. This roughly indicates the PCBs found were recently deposited and are probably still accumulating, although the sedimentation rates were not determined. Studies in the Santa Barbara Basin suggest that a substantial portion of the chlorinated hydrocarbons entering the sea from diverse sources is being deposited in the sediments (94). Also, data gathered from the major drainage basins of the United States indicate widespread occurrence of PCBs in bottom sediments (95). The data also reinforce the statement that PCBs are associated with solids and that efficient suspended solids removal is important in treating wastes for chloro-organic compounds.

CLAMS

A total of 74 clams (Anodontoides ferussacianus) were placed at 10 locations along the Fox River and in Green Bay to determine the potential bioaccumulation of PCBs. Three original specimens were analyzed as control specimens for chloro-organic compounds. All were below the limit of analytical detectability for the chloro-organics screened during this project. Fifteen clams were retrieved from 4 locations for chloro-organic analysis. The remaining clams were lost to either vandalism or lack of survival. Table 14 presents the data obtained, and Figure 37 illustrates the relationship of PCB uptake to time.

Table 14. PCB Analysis of Clams* Placed in the Fox River

Location	Date Placed	Date Recovered	Days in Place	Clams Retrieved	PCB (ug/kg)
1. Green Bay	5/25/77	6/3/77	9	2	260
2. 0.5 mile above Wrightstown	5/24/77	6/3/77	10	2	240
3. 0.5 mile above Wrightstown	5/24/77	6/3/77	10	1	250
4. Green Bay	5/25/77	6/22/77	27	2	740
5. Below Depere Dam	5/24/77	6/22/77	28	2	255
6. 0.5 mile above Wrightstown	5/24/77	6/22/77	28	2	300
7. 0.2 mile below Appleton STP	5/24/77	6/22/77	28	4	600

*_Anodontoides ferussacianus_

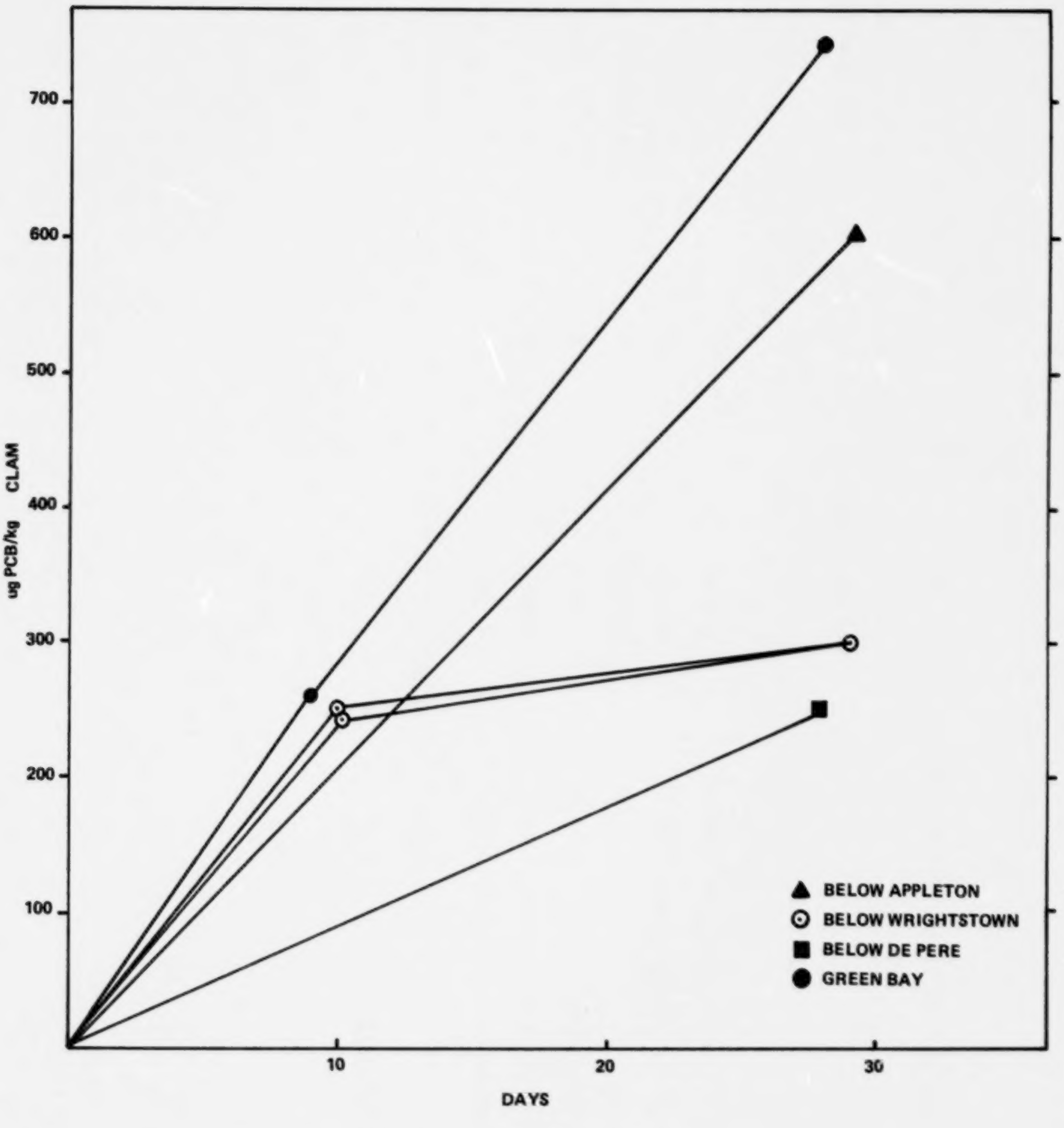

Figure 37. PCB Bioaccumulation in Clam Tissue

The original intent of this portion of the study was to take two or three clams from each site at various time intervals over a 3 month period for PCB analysis. This procedure should have indicated a rate and a maximum range of PCB bioaccumulation in the Fox River system. The loss of most of the clams was disappointing, but the data obtained do indicate that PCBs bioaccumulate in clams at a rapid rate. The mean uptake rate for the samples collected below DePere and above Wrightstown was 10 ug/day for 28 days. The mean uptake rate for the Appleton and Green Bay samples was 24 ug/day for 28 days. The data on chloro-organics in sediment (Table 12) indicates the higher PCB uptake in clam locations also have higher sediment concentrations. This tends to indicate the uptake rate of PCBs is related to the concentration of PCBs in the sediments.

A more detailed study would be required to firmly establish a relationship between uptake rate, maximum bioaccumulation, sediment concentration, and water concentration. There is no way to determine from this study if the source of PCBs was from new material or from PCBs already present in the sediment.

An attempt was made to analyze clam tissue for compounds other than PCBs; however, the lab methods could not be finalized during the time period available. Tentative identification of pentachloroanisole (PCA) was made on two samples from above Wrightstown. The PCA could not be reliably quantified because the apparent concentration of 0.005 ug/kg was too low for GC/MS analysis.

The data obtained on clam tissue indicate that clams are an excellent indicator organism for chloro-organic compounds, as indicated by other studies (96, 9). Live clams are rarely found in the Fox River and the eastern portion of Lower Green Bay. This may be due to bioaccumulation of toxic substances in conjunction with low dissolved oxygen concentrations. Dissolved oxygen concentrations are improving due to improved waste treatment; however, the clam population may not be able to return due to the polluted nature of the bottom sediments.

FISH

Polychlorinated biphenyls in the environment can cause a variety of problems. One of the most important is their effect on the fishery. High concentrations of PCBs are toxic to fish, but of greater significance is chronic exposure resulting from the consumption of contaminated fish by higher vertebrates including man. The U.S. Food and Drug Administration tolerance level for PCBs in the edible portion of fish is 5 ppm, and a lower level of 2 ppm has been proposed (88). The Canadian Food and Drug Directorate tolerance level is 2 ppm (88).

Thirty-five fish fillet samples were analyzed and all contained quantifiable PCB concentrations. The detailed data are found in Table 15. PCB concentrations found in fish below the DePere Dam ranged from 0.4 mg/kg in a bowfin to 90 mg/kg in a carp. Sixteen of the 35 samples exceeded the FDA tolerance of 5 mg/kg. Fish from Little Lake Butte des Morts contained higher PCB concentrations than fish from DePere. However, the sizes and fat content of Little Lake Butte des Morts fish were generally

Table 15. Lower Fox River Fish Sampling and Analysis Results

Sample Location	Date	Common Name	Length (mm)	% Fat	PCB* (mg/kg)	Other Chloro-organics (mg/kg)
Little Lake Butte des Morts	April 77	N. Pike	688.3	0.5	2.4 (1242)	PCA <0.005
		N. Pike	769.6	0.8	2.3 (1242)	PCA 0.020
		Walleye	411.5	1.5	1.8 (1242)	PCA = 0.060
		Walleye	424.2	2.4	5.2 (1242)	PCA = 0.036
		Carp	406.4	1.2	2.7	
		Carp	444.5	1.7	10.0 (1242)	PCA <0.010
		Carp	406.4	2.0	4.3 (1242)	Dieldrin <0.010
		Carp	469.9	2.3	13.0 (1242)	
		Carp	546.1	4.6	16.0 (1248)	
		Carp	584.2	5.4	28.0 (1242)	
		Carp	558.2	5.8	30.0 (1242)	
		Carp	508.0	6.1	18.0	
		Carp	533.4	6.1	20.0 (1242)	
		Carp	596.9	9.0	39.0 (1242)	
	(5)	Carp	$\bar{X}$=518.6	12.5	50.0 (1242)	
Below DePere Dam	April 77	N. Pike	454.7	0.5	2.5 (124)	
		N. Pike	530.9	0.7	3.2 (1248)	
		N. Pike	497.8	1.0	3.0	
		Walleye	452.1	2.6	6.8 (1248)	
		Walleye	330.2	4.9	4.5 (1248)	
		Bowfin	647.7	0.4	0.5	Dieldrin< 0.010
	(5)	Y. Perch	$\bar{X}$=203.7	1.0	1.0 (1248)	
	(5)	Y. Perch	$\bar{X}$=196.9	2.6	5.3 (1248)	
	(4)	Y. Perch	$\bar{X}$=171.5	2.8	6.6 (1248)	
	(5)	Y. Perch	$\bar{X}$=184.9	3.2	5.4 (1248)	
		W. Sucker	429.3	0.6	1.4	
		W. Sucker	482.6	0.6	2.5 (1248)	Dieldrin 0.008

Table 15. Continued

	Date	Common Name	Length (mm)	% Fat	PCB* (mg/kg)	Other Chloro-organics (mg/kg)
Below DePere		W. Sucker	482.6	1.0	2.3 (1248)	Dieldrin<0.010
		W. Sucker	381	1.0	4.4 (1248)	Dieldrin 0.012
		W. Sucker	452.1	1.8	3.2	Dieldrin 0.010
		W. Sucker	431.8	2.3	4.2	Dieldrin 0.022
		Carp	439.4	0.7	2.5 (1248/1254)	Dieldrin<0.010
		Carp	325.1	1.6	6.6 (1248)	
		Carp	259.1	6.9	4.4 (1242)	
		Carp	375.9	9.0	90.0 (1248)	

* Number in parentheses indicates Aroclor mixture most similar to the PCBs in sample.

greater than DePere fish, which may partially account for their greater level of PCBs. If fish of the same approximate length and fat content are compared, little difference is apparent. This study supports the findings of others that high fat content fish, such as carp, contain higher concentrations of PCBs (97). PCBs are fat soluble and thus tend to accumulate in fat tissue. Figure 38 is a regression analysis of the correlation between fat content and PCB concentrations for all the various species sampled.

The data indicate Fox River fish accumulate significant quantities of PCBs. However, the effect of PCBs on organisms in the Fox River ecosystem cannot be determined from this study.

An attempt was made to identify and quantify compounds other than PCBs in fish tissue, but the same analytical problems encountered with clam tissue were experienced with fish. The presence of PCA in a range of 20 to 60 ug/kg in walleye and northern pike tissue from Little Lake Butte des Morts was verified. Laboratory studies have shown that PCA is readily accumulated from water by fish and is retained in fish tissue for days after contaminated specimens are placed in PCA-free environment (98). Chemical extraction losses were thought to be significant for PCA in fish tissue. Therefore, higher concentrations of PCA and the presence of other organic compounds are probable. The insecticide Dieldrin was occasionally found in the 0.008-0.022 mg/kg range below the DePere Dam.

Because of the free movement of fish, correlation between tissue concentrations and location may not be valid. However, the flow of the Fox River is controlled by a series of dams that restrict fish movement. In addition

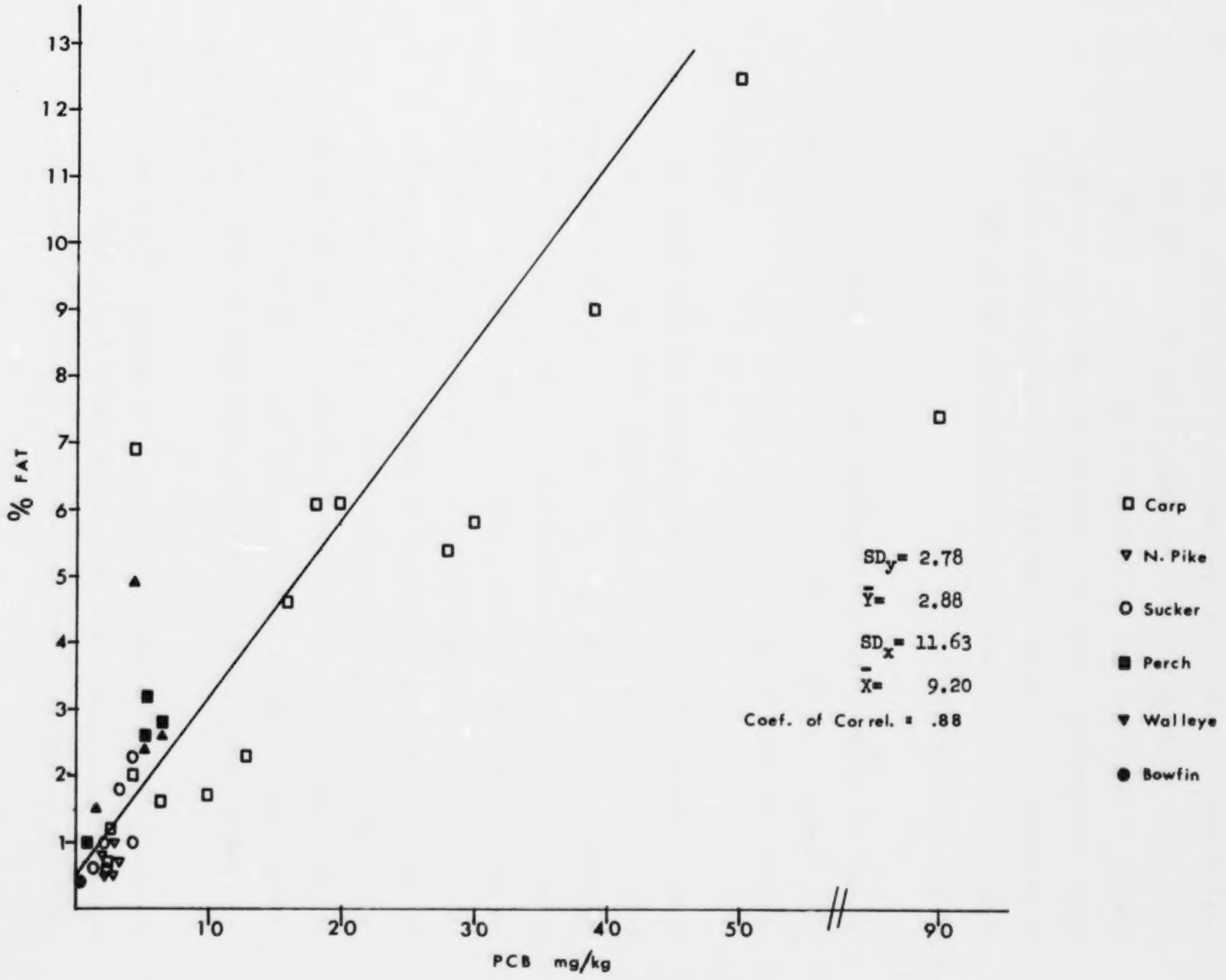

Figure 38. Correlation of PCB Concentration to Fat Content in Fish

there are no other significant point sources of chlorinated organics in the area under investigation. It appears valid to assume most chlorinated organic compounds found in fish tissue originated from sources discharging to the Fox River.

The PCB data in Table 15 indicate the commercial mixture most similar to the PCB found in the fish sample. Aroclor 1242 was predominant in Little Lake Butte des Morts fish, while Aroclor 1248 was the major mixture in fish at the sampling site below the DePere Dam. Chromatograms of 1242 and 1248 are very similar in component peaks and are differentiated by relative peak heights. Thus the presence of 1248 or a more highly chlorinated mixture such as 1254 in the sample could mask the presence of 1242. The presence of 1248 in the fish at the downstream site (DePere) may indicate the presence of a source of one of the PCB mixtures with more chlorine than 1242. In fact this has been observed in the present investigation. Table 3 indicates several sources of Arocolor 1248 or 1254 that could introduce these mixtures to the downstream fish. Also, biological mechanisms may alter the components of 1242, making it appear as 1248 when chromatographed.

SNOWMELT

Contributions of chlorinated hydrocarbons to surface waters may be derived from atmospheric deposition. The importance of precipitation scavenging and aerial deposition as a source of these substances has not been fully addressed. However, atmospheric transport was an important route for spreading the organo-chlorine DDT throughout the biosphere(13,14). Additional recent studies indicate atmospheric inputs as the present major source of PCBs to Lake Michigan at a rate of 5,000 kilograms per year (15) perhaps because Lake Michigan's drainage basin is small compared to the surface area of the lake. However, most river systems display the reverse relationship. In the Fox-Wolf River system the ratio of water surface to drainage basin is less than 6 percent. Thus, direct additions of atmospheric pollutants to the river are not as great as the amount potentially delivered by runoff.

Snow was collected to yield a quantitative estimate of chloro-organics entering the river system by land runoff of melted snow. This kind of sample was chosen because:

1. Snow forms a ground cover that may collect chloro-organic deposition. Thus, snow should contain an integration of all the impacted chlorinated hydrocarbons during the lifetime of the layer.

2. Snow may contain the precipitation scavenged fraction of chloro-organics as well as chloro-organics adhering to particulates originating from local windblown sources.

3. PCBs and similar compounds are relatively insoluble in water under most natural conditions. Thus, analyses of runoff may not indicate the most significant fraction of these substances moving through the environment. Therefore, snow sampling appeared to be an attractive method for measuring chloro-organics available for runoff events.

A total of 19 snowmelt collections were made during January and February of 1977 in the Fox-Wolf River drainage basin. Locations are shown by Figures 39 and 40. More intensive sampling was conducted in the City of

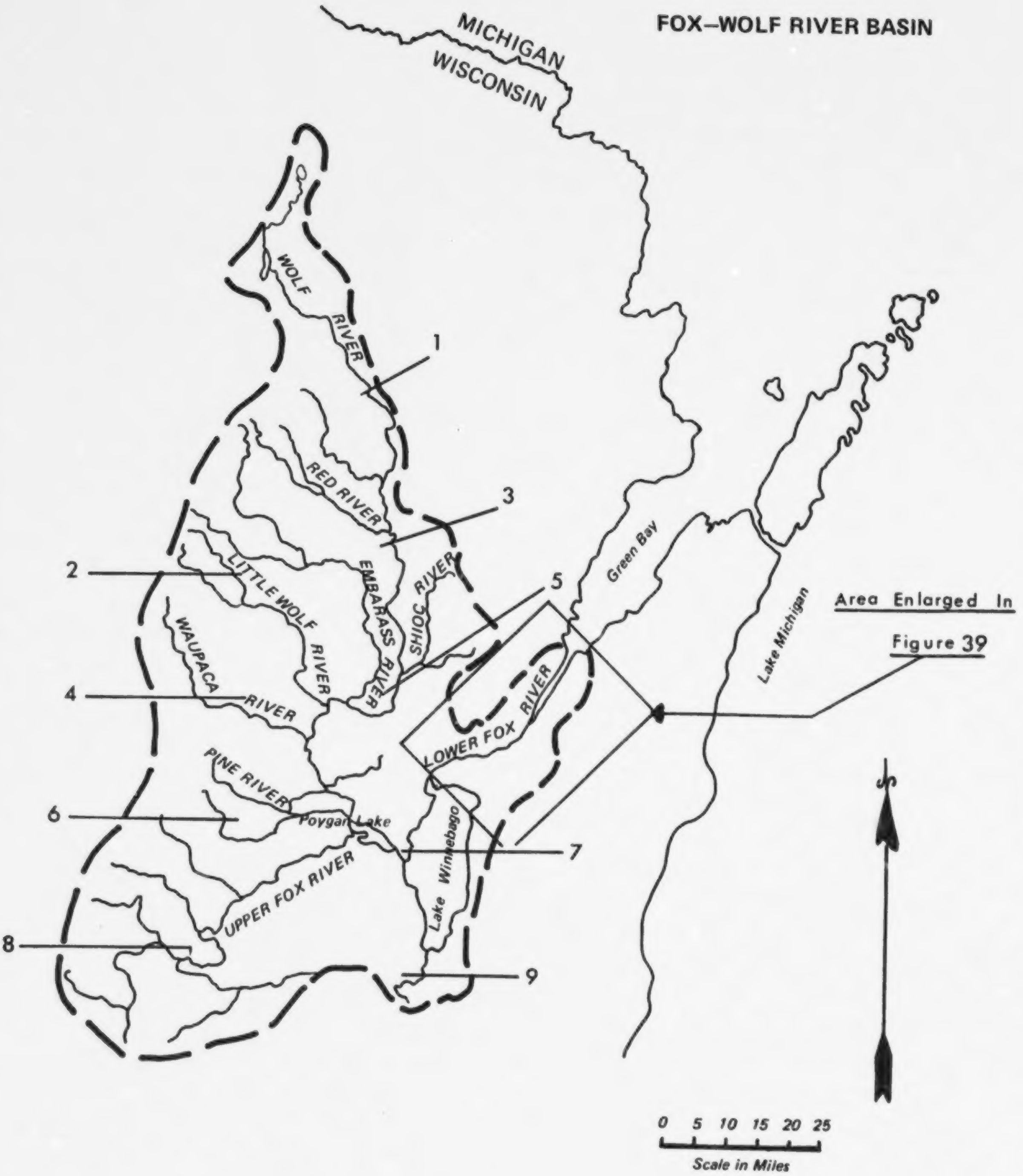
FOX–WOLF RIVER BASIN
MICHIGAN
WISCONSIN
WOLF RIVER
1
RED RIVER
3
2
LITTLE WOLF RIVER
EMBARASS RIVER
SHIOC RIVER
5
Green Bay
Area Enlarged In Figure 39
Lake Michigan
WAUPACA RIVER
4
LOWER FOX RIVER
PINE RIVER
6
Poygan Lake
7
Lake Winnebago
UPPER FOX RIVER
8
9
0 5 10 15 20 25
Scale in Miles

Figure 39. Snow Sampling Locations

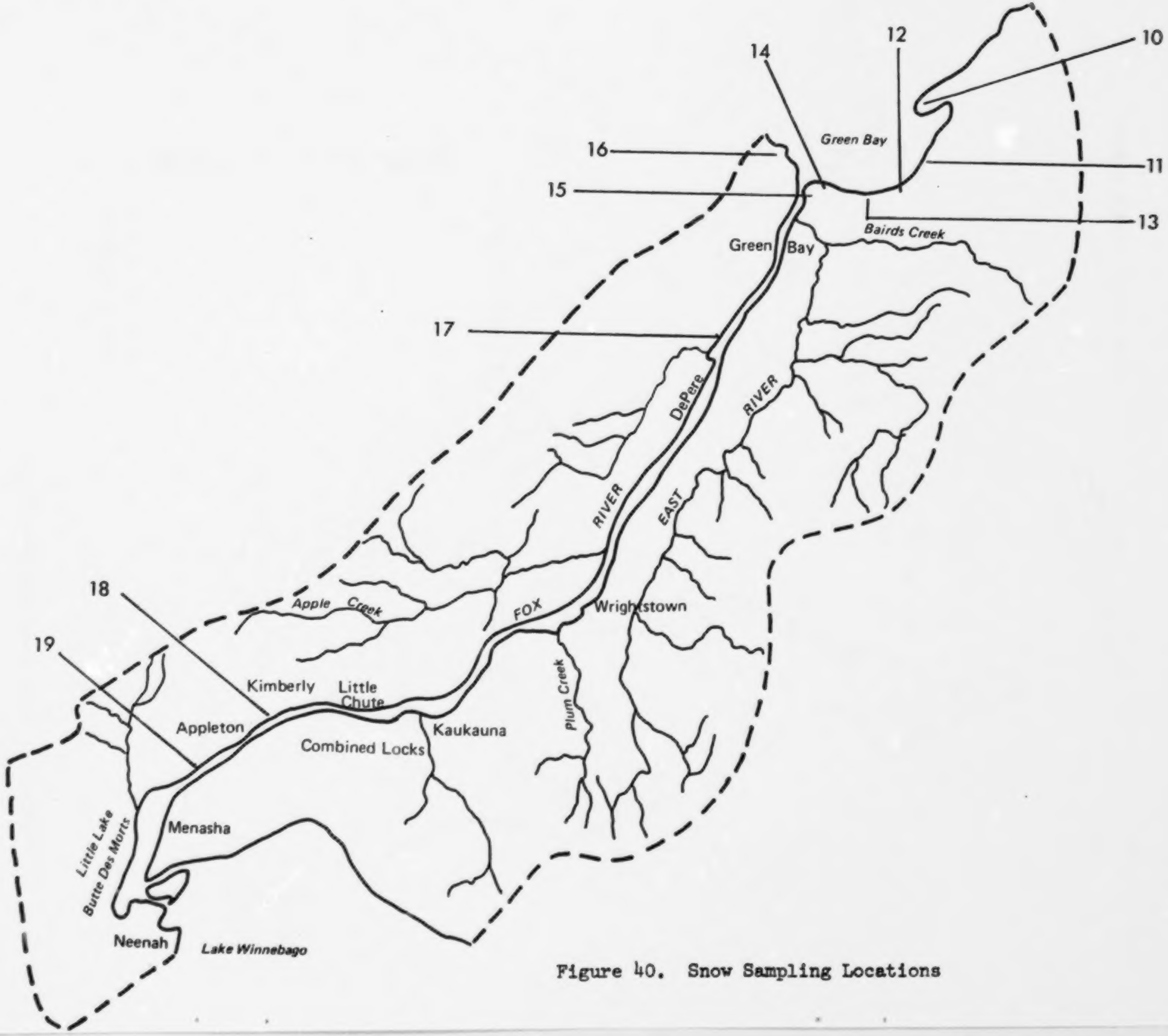
10
11
12
13
14
15
16
17
18
19
Green Bay
Bairds Creek
Green Bay
RIVER
EAST
DePere
RIVER
FOX
Wrightstown
Plum Creek
Apple Creek
Kimberly
Little Chute
Kaukauna
Combined Locks
Appleton
Menasha
Little Lake Butte Des Morts
Neenah
Lake Winnebago

Figure 40. Snow Sampling Locations

Green Bay vicinity because of its industrial nature and varied sources of chloro-organics. Approximately half the collections were made away from the urban areas in the basin. The results of PCB measurements are presented in Table 16. There was no effort to measure other chloro-organics in snowmelt.

Table 16. Results of PCB analysis on snowmelt samples from the Fox-Wolf River drainage basin.

Sample Number	PCB Microgram/liter
1	< 0.2
2	< 0.2
3	< 0.5
4	0.15
5	< 0.1
6	< 0.1
7	< 0.2
8	< 0.1
9	< 0.2
10	< 0.2
11	< 0.2
12	< 0.2
13	< 0.2
14	< 0.2
15	< 0.2
16	< 0.2
17	< 0.2
18	< 0.2
19	< 0.2

It is difficult to make conclusions on the significance of chloro-organics levels in snowmelt when all analyses except one yielded PCB concentrations less than the analytical/detection limit. The one reported PCB concentration was just at the detection limit, and this indicates other samples may have contaminated PCBs, but at very low concentrations.

Therefore, it is impossible to compare sample locations, since all results were essentially the same. But it is useful to compare these data with the results of similar investigations in the area.

In a separate study conducted during March of 1976, the Wisconsin DNR collected eight snowmelt samples in the Lower Fox Valley, from Neenah to Green Bay (16). Collection methods and sample size were similar to those used in this study. The results indicated levels less than 0.1 ug PCB/L of snowmelt in all samples except one, which was reported at less than 0.2 ug/L. The difference between these detection levels is not significant. Thus, for 2 consecutive years, PCBs were not detected in 2-2.5 liters of snowmelt from the Lower Fox River Valley. However, in larger volumes of snow sampled in the Chicago area, PCBs were consistently detected in four samples(15). In the Chicago investigation, enough snow was melted to yield 6 - 12.7 liters of water. Concentrations of PCBs ranged from 0.0601 to 0.3272 ug/L. These concentrations were just at or below the level of detectability. The ability to report these small concentrations reflects the extraction of a larger sample size. A significant finding of the same investigation was that the concentration of PCBs in precipitation (rainfall) was as high in northern Michigan as it was in Chicago. These concentrations were found in the range of 0.1 - 0.2 ug/L by extracting 1.3 - 77.5 liters of water.

In another study conducted at Isle Royale National Park in Lake Superior, concentrations of 0.230 ug PCB/L were found in snow samples(17).

The following data from a 1975 snowmelt study conducted in Wisconsin (18) indicated PCBs were present in snow.

Table 17. PCB Levels in Snowmelt Water, 1975(18)*

City	PCB (micrograms per liter)
Green Bay	0.01
Grafton	(None Detected)
Kewaskum	(None Detected)
Racine	0.17
Kenosha	0.22
Madison	0.24
Milwaukee	0.20

*Sampling methods and sample volumes were not reported.

The question of snowmelt samples representing precipitation is open to discussion. There is no well-defined correlation between levels of PCBs in snow cover and levels in precipitation. However, the data will indicate the amount of PCBs available for land runoff during storm events or melt periods that may eventually be channelled into the area of investigation.

PCBs are found in similar concentrations at many locations, so it is likely they are dispersed by atmospheric transport mechanisms. Because these locations bracket the Fox-Wolf River drainage system, it is reasonable to suspect PCBs are present in the precipitation and snow covering the area. Although a great majority of the data from this study did not indicate the presence of PCBs, there is reason to suspect the sample size was not adequate for analyses.

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APPENDIX A

COMPOUNDS IDENTIFIED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Explanation of table symbols

COMPOUND:

CD - if on the Environmental Protection Agency's Consent Decree Priority Pollutant List
P - Denotes having previously been reported in paper mill wastes
P/T - Denotes toxic compounds from paper mill wastes
Listed alphabetically except when grouped under Fatty Acids, Fatty Acid Methyl Esters, Resin Acids, Resin Acid Methyl Esters, Resin Acids - Chlorinated, and Resin Acid Methyl Esters - Chlorinated
Listed as detected unless otherwise noted

DISCHARGER: See next page for list of industrial/municipal wastewaters, biota, or sediment analyzed by GC/MS

LOCATION:

a	Denotes raw wastewater
b	Denotes after primary clarifier effluent
c	Denotes lagoon effluent
d	Denotes final effluent

EXTRACT:

1	pH greater than 11, methylene chloride-hexane; hexane or 94% hexane/6% ethyl ether florisil eluate
2	pH greater than 11, methylene chloride-hexane; 80% hexane/20% ethyl ether florisil eluate
3	pH less than 3, chloroform redissolved in acetone
4	pH less than 3, chloroform redissolved in acetone, methylated with methyl iodide and re-extracted into hexane
5	pH less than 3, chloroform redissolved in acetone - without any prior basic extraction (1 sample)

IDENTIFICATION:

Lit. No. Denotes literature reference of mass spectrum used to compare with that from sample analysis
8 Pk Index Denotes Eight Peak Index of Mass Spectra, 2nd ed., 1974 -- 8 most abundant ions from literature compared with that from sample analysis
Standard A denotes commercially available compound
Standard B denotes compound synthesized in our laboratory
Standard C denotes compound furnished by others previously reporting it

LITERATURE - PREVIOUS CITATION(S) OF COMPOUND:

(Ref. No., page) Number Listed in Bibliography (in cases of extensive citations, only representative references are given). Almost all compounds detected in this study were cited in reference 50, which is only included in this table whenever no other references are listed for a compound.

SAMPLES ANALYZED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

ENVIRONMENTAL MATRIX	LOCATION	EXTRACT
Industrial/municipal Wastewaters		
1. Kimberly-Clark, Badger Globe, Neenah Papers	b	2 & 4
	d	1
	d	3
2. Bergstrom Paper Company	a	1
	a	1
	a	1
	a	1
	a	2
	b	2
	d	1
	d	2
	d	3 & 4
3. Neenah-Menasha Sewage Treatment Plant	d	4
11. Consolidated Paper Company	a	3 & 4
	d	5
12. Appleton Sewage Treatment Plant	a	3
	d	3
14. Kimberly Sewage Treatment Plant	d	1
16. NCR Appleton Papers	a	3 & 4
	b	2
	d	1
	d	2
	d	3
17. Thilmany Pulp & Paper Company	d	1
	d	4
20. Wrightstown Sewage Treatment Plant	d	2
24. American Can Company	c	2
25. Proctor & Gamble Company (Charmin)	a	1
	a	1
	a	2
	a	3
	a	3
Biota		
Carp		1
Carp		1
Carp		2
Sediment		1

APPENDIX A

COMPOUNDS IDENTIFIED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Available mass spectra of these compounds appear in Appendices D & E

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
CD	Acenapthene	2	b	2	Lit. 47, p. 79	(41,692), (33,62)
	Acetone, Tetrachloro-	11	d	5	8 Pk Index	(42,251), (43,363)
P	Acetovanillone	11	d	5	Standard A	(44,650), (45,28)
		16	a	3		(46,246)
		17	d	3		
	Aniline, Trichloro-	1	b	2	Standard A	(47,165)
		2	b	2		
	Anisole, Pentachloro-	1	b	2	Standard A	(43,333), (48,582-3)
		17	d	1		
CD	Anthracene (or Phenanthrene ?)	1	b	2	Standard A	(41,692), (49,443)
	Benzene, Dichloro-diethyl-		carp	1	8 Pk Index	NONE(?)
	Benzoate, Dimethyl	11	d	5	8 Pk Index	NONE(?)
	Benzoate, Methyl methoxy-	11	d	5	8 Pk Index	(50,11)
		16	a	4		
	Benzoic acid	12	a	3	8 Pk Index	(51,525), (48,593)
		16	a	3		(52,124), (53,392)
	Benzoic acid, [methyl ester derivative]	16	a	4	8 Pk Index	
	Benzoic acid, Isopropyl- [methyl ester derivative]	11	a	4	8 Pk Index	NONE(?)
	Benzophenanthrene, Methyl- (or Benzanthracene, Methyl-?)	1	b	2	Lit. 47, p. 81	(41,691), (42,443)
	Benzophenone	25	a	2	8 Pk Index	(48,583)

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
	Benzothiazole	1	b	4	Standard A	(53,389), (33,64)
	(10-30 ug/L in final effluents)	1	d	3		
		2	a	2		
		2	d	3 & 4		
		12	d	3		
		16	b	2		
		16	a	3		
		16	d	2		
		17	d	3		
		25	a	3		
	Benzothiazole, Hydroxy-	1	d	3	Standard A	NONE(?)
	(10-30 ug/L in final effluents)	16	a	3		
		17	d	3		
	Benzothiazole, Hydroxy- [methyl ether derivative]	2	d	4		
P	Benzothiazole, Methyl Thio-	1	b	4	Standard A	(54,211), (45,28) (53,392)
	(10-40 ug/L in final effluents)	1	d	3		
		2	d	4		
		16	a	4		
		16	b	2		
		16	d	1		
		16	d	2		
		17	d	3 & 4		
P	Benzyl alcohol	16	a	3	8 Pk Index	(49,440), (51,525), (45,74)
	Biphenyl	2	a	1	8 Pk Index	(41,692)
	Biphenyl, Methyl-	2	a	1	8 Pk Index	(41,692)
	Bisphenol A [dimethyl ether derivative] (4,4' Isopropylidene diphenol)	2	d	4	Standard A	(55,695)
	Bisphenol A, Chloro- [dimethyl ether derivative] (MW 290)	2	d	4	Interpret.	NONE(?)
	Bisphenol A, Dichloro- [dimethyl ether derivative] (MW 324) (2 isomers	2	d	4	Interpret.	Chem. Abs. 82:155630x

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
	Bisphenol A, Tetrachloro- [dimethyl ether derivative] (MW 392)	2	d	4	Interpret.	Chem. Abs. 82:155630x
	Bisphenol A, Trichloro- [dimethyl ether derivative] (MW 358)	2	d	4	Interpret.	NONE(?)
	Borneol, Iso-	11	d	5	8 Pk Index	(50,13)
P	Caffeine	12	a	3	Standard A	(52,122), (51,526)
	Camphor, Oxo-	11	d	5	8 Pk Index	NONE(?)
	Carbazole	1	b	2	8 Pk Index	(33,65)
CD	Chlordane (isomer ?)	2	a carp	1 2	Standard A	(56,280), (57) (43,356), (58,333)
CD	Chrysene	1	b	2	Standard A	(49,443), (41,692)
CD	DDD		2 carp	1	Standard A	(56,280)
CD	DDE		2 carp	1	Standard A	(58,333), (43,357) (56,280)
CD	DDT		carp	1	Standard A	(58,333)
P	Dodecane	25	a	1	8 Pk Index	(53,389), (33,70) (43,357)
	FATTY ACIDS					
P	Heptadecanoic Acid [methyl ester derivative]	2	d	4	Standard A	(33,75), (44,651), (45,28) (51,524)
P	Lauric Acid	12	a	3	8 Pk Index	(31,21), (51,524)
P	Myristic Acid	12	a	3	8 Pk Index	(33,77), (44), (31,21) (51,524), (45,27)
P/T	Oleic Acid [methyl ester derivative]	2	d	4	8 Pk Index	(33,79) (59) (44) (51,524) (60,37) (28)
P	Palmitic Acid	12	a	3	8 Pk Index	(33,79) (44) (51,524) (31,21) (61)
	Palmitic Acid [methyl ester derivative]	2	d	4	Standard A	

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
P	Stearic Acid	12	a	3	8 Pk Index	(61) (44) (51,524) (60,37 (31,21)
	Stearic Acid [methyl ester derivative]	2	d	4	Standard A	
	FATTY ACID METHYL ESTERS:					
P	Palmitate, Methyl-	2	a	2	Standard A	(50,26)
P	Stearate, Methyl-	24 2 12	c a a	2 2 3	Standard A	(50,33)
CD	Fluoranthene	1	b	2	Standard A	(43,443) (41,692) (33,71)
P	Guaiacol	11 17	d d	5 3	Standard A	(44,650) (60,28) (45,27) (33,72)
P/T	Guaiacol, Dichloro- (2 isomers) (2 isomers)	11 11	d a	5 3	Standard C	(61) (36,19) (46,246)
	Guaiacol, Dichloro- [methyl ether derivative] (3 isomers)	11	a	4		
P/T	Guaiacol, Tetrachloro- (10-50 u g/L in final effluents)	2 11	d d	3 5	Standard C	(59) (62) (23-26) (28) (46,246)
	Guaiacol, Tetrachloro- [methyl ether derivative]	2 11	d a	4 4	Standard C	
P/T	Guaiacol, Trichloro- (1 isomer) (10-60 u g/L in final effluents) (2 isomers) (3 isomers)	2 11 11	d a d	3 3 5	Standard C	(59) (44,650) (62) (23-26) (36,19) (63) (28) (31) (46,246)
	Guaiacol, Trichloro- [methyl ether derivative] (1 isomer) (2 isomers)	2 11	d a	4 4	Standard C	
	Heptadecane	 16	2 carp d	1 1	8 Pk Index	(49,445) (36,19) (31)
CD	Hexachlorocyclohexane (lindane)	14	d	1	Standard A	(56,280)
CD	Hexachlorocyclopentadiene	2	a	1	Standard A	(57,736)

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No., page)
	Hexadecane	16	d	1	8 Pk Index	(49,445) (33,73)
		2	d	3		
	Indole, Chloro- (isomer ?)	20	d	2	Standard A	Chem. Abs. 83:131403v
	p-Menth-4ene-3-one	11	d	5	8 Pk Index	NONE(?)
	Naphthalene, Isopropyl-	25	a	1	8 Pk Index	(33,75)
	Naphthalene, Methyl-	2	b	2	8 Pk Index	(49,440) (43,358) (33,76) (53,392)
	Nonadecane	2	a	1	8 Pk Index	(33,78)
		16	d	1		
	Octadecane	2	d	3	8 Pk Index	(49,445) (33,79)
		16	d	1		
P	Pentadecane	2	a	1	8 Pk Index	(43,359) (33,80-1)
		2	d	3		
		16	d	1		
	Phenanthrene, Methyl-	1	b	2	8 Pk Index	(49,443) (41, 692) (33,76)
CD	Phenol	2	a	2	Standard A	
		2	d	3		(64,315) (45,27)
		17	d	3		
		12	a	3		(33,81) (44,650)
		12	d	3		
		16	a	3		
		1	d	3		
	Phenol, p-Tertiary Amyl-	16	b	2	8 Pk Index	NONE(?)
CD	Phenol, Chloro- [methyl ether derivative]	2	d	4	8 Pk Index	(52,140)
	Phenol, p-(α-chloroethyl)-	16	d	3	8 Pk Index	NONE(?)
	Phenol, Decyl-	1	d	3	8 Pk Index	(54,211)
		17	d	3		
CD	Phenol, Dichloro- (1 isomer)	2	d	3	Standard A	
	(15-40 ug/L in (2 isomers)	11	d	5		
	final effluents) (2 isomers)	16	a	3		
	Phenol, Dichloro- [methyl ether derivative]	2	d	4	Standard A	(36,19)
		11	a	4		

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No., page)
P	Phenol, Ethyl- (isomer?)	11	d	5	8 Pk Index	(33,71)
		16	a	3		
	Phenol, Nonyl- (or Butylated Hydroxytoluene)	2	d	2	8 Pk Index	(33,78-9)
		16	b	2		
		1	d	3		
	(3 isomers)	17	d	3		
	(3 isomers)	2	d	3		
	Phenol, Nonyl- [methyl ether derivative] (3 isomers)	2	d	4		
CD	Phenol, Pentachloro-	11	d	5	Standard A	(33,80) (51,525)
		12	a	3		
		2	d	3		(58,333) (55,697)
		17	d	3		
	Phenol, Pentachloro- [methyl ether derivative]	2	d	4	Standard A	
		17	d	4		
		3	d	4		
	Phenol, Tetrachloro-2,3,4,6 or 2,3,5,6 isomer	11	d	5	Standard A	(33,83) (42,251) (58,333)
		11	a	3		
	Phenol, Tetrachloro- [methyl ether derivative] (2-20 ug/L in final effluents)	11	a	4	Standard A	
		2	d	4		
		17	d	4		
		1	b	4		
		3	d	4		
	Phenol, Trichloro- (isomer ?) (5-100 ug/L in final effluents)	12	d	3		
		11	a	3		(58,333) (53,389) (42,251)
	Phenol, Trichloro- [methyl ether derivative] (1 isomer)	11	a	4		
	(2 isomers)	3	d	4		
	Phenol, 2,4,5 or 2,3,4 Trichloro-	17	d	3	Standard A	
		12	a	3		

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
	Phenol, 2,4,5 or 2,3,4 Trichloro [methyl ether derivative]	17	d	4	Standard A	
CD	Phenol, 2,4,6 Trichloro	16	a	3	Standard A	(62) (36,19) (46,246) (53,392)
		11	d	5		
		2	d	3		
	Phenol, 2,4,6 Trichloro- [methyl ether derivative]	2	d	4	Standard A	
		16	a	4		
	Phenol, Trichloro-dimethoxy-	2	d	3	Interpretation	NONE(?)
	Phenol, Trichloro-dimethoxy- [methyl ether derivative]	2	d	4	Interpretation	NONE(?)
	Phenol, Undecyl-	1	d	3	8 Pk Index	NONE(?)
		17	d	3		
		2	d	3		
	Phenyl Decane	2	a	1	8 Pk Index	NONE(?)
		2	a	1		
		2	a	1		
			carp	1		
		12	a	3		
	Phenyl dodecane	2	a	1	8 Pk Index	NONE(?)
		2	a	1		
		2	a	1		
		2	d	3		
			carp	1		
		12	a	3		
	Phenyl Undecane	2	a	1	8 Pk Index	NONE(?)
		2	a	1		
		2	d	3		
			carp	1		
		12	a	3		
	Phosphate, Tributyl-	12	d	3	8 Pk Index	(49,445) (53,387) (43,363)
		2	d	3 & 4		

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No., page)
CD	Phthalate, Dibutyl-	1	b	2	Lit. 47, p. 88	(49,445) (51,525) (56,283)
		12	a	3		
CD	Phthalate, Diethyl-	25	a	1	Lit. 47, p. 88	(51,525)
		25	a	2		
CD	Phthalate, Dioctyl- (isomer ?)		carp	1	Standard A	(51,525) (48,583) (61,833) (56,283)
		24	c	2		
		2	a	2		
		2	d	3 & 4		
		16	d	2		
		12	a	3		
		12	d	3 & 4		
		25	a	3		
CD	Polychlorinated Biphenyls (2-7 chlorine isomers)	2	a	1	Standard A	(65); (66); (67) (68) (49,441) (69)
		2	d	1		
		2	a	1		
		2	a	1		
			2 carp	1		
			sediment	1		
			carp	2		
		2	b	2		
P	Propan-2-one, 1-(4-hydroxy-3-methoxy phenyl) (or guaiacyl acetone)	11	a	3	8 Pk Index	(50,30)
CD	Pyrene	1	b	2	Standard A	(49,443) (41,692)
	RESIN ACIDS					
P/T	6,8,11,13 Abietatetraen-18-oic Acid, [methyl ester derivative] (MW 312)	2	d	4	Lit. 72 & (45, 151)	(33,62) (44,650) (45,29)
P/T	Dehydroabietic Acid, (MW 300) (100-8500 u.g/L in final effluents)	2	d	3	Standard C	(70), (61) (44) (21) (29,4) (59) (60,37) (45,29) (33,66-7) (23-28) (30) (31,21) (71)
		11	d	5		
		11	a	3		
	Dehydroabietic Acid [methyl ester derivative] (MW 314)	2	d	4	Standard C	
		17	d	4		
		16	a	4		
		11	a	4		

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
P/T	8,15 Isopimardien-18-oic Acid, [methyl ester derivative] (MW 316)	2	d	4	Lit. 72	(29,3)
P/T	Oxo-dehydroabietic Acid, [methyl ester derivative] (MW 328)	2	d	4	Lit. 61, 835	(61) (24,35 + 59) (29,21)
	Pimaric Acid (MW=302)	2	d	3		(45,29) (27) (28) (29,4) (30) (59) (60,37)
P/T	Pimaric Acid, [methyl ester derivative] (MW 316)	2	d	4	Lit. 72 & (45,49)	
P/T	Sandaracopimaric Acid, [methyl ester derivative] (MW 316)	2	d	4	Lit. 72 & (45,50)	(61) (60,37) (45,29) (27) (28) (29,4) (30)
	RESIN ACID, METHYL ESTERS:					
P/T	Methyl dehydroabietate	24 11	c d	2 5	Standard C	(27,130)
	RESIN ACIDS, CHLORINATED:					
P/T	Chlorodehydroabietic Acid, [methyl ester derivative] (MW 348) (2 isomers)	2	d	4	Standard C	(59) (23-26) (28) (63)
P/T	Dichlorodehydroabietic Acid, [methyl ester derivative] (MW 382)	2	d	4	Standard C	(59) (23-26) (28) (63)
	RESIN ACID METHYL ESTERS, CHLORINATED:					
	Chlorodehydroabietate, Methyl	24	c	2	Standard C	NONE (?)
	Dichlorodehydroabietate, Methyl	24	c	2	Standard C	NONE (?)
P	Salicylic Acid, [methyl ester derivative]	16	a	4	8 Pk Index	(51, 526)
P	Syringaldehyde	11 16 25	d a a	5 3 & 4 3	Standard A	(33,83) (45,28)

	COMPOUND	DISCHARGER	LOCATION	EXTRACT	IDENTIFICATION	LITERATURE (Ref. No.,page)
	Syringaldehyde, Chloro-	25	a	3	Standard B	NONE?
P	Tetradecane	16	d	1	8 Pk Index	(33,84) (43, 359)
	Toluene, Dichloro-	2	d	1	Standard A	(42,251)
	Toluene, Trichloro-	2	d	1	Standard A	NONE?
		2	a	1		
P	Vanillin	2	d	3	Standard A	(44,650) (45,28) (46,246) (33,85)
		11	d	5		
		17	d	3		
		16	a	3		
		11	a	3		
		25	a	3		
P	Vanillic Acid, [methyl ester derivative]	17	d	4	8 Pk Index	(45,28) (55,697) (46,246)
P	Veratrole, Dichloro- (isomer ?) or (Dimethoxybenzene, Dichloro-)	1	b	2	Lit. 61, p. 835	(47,102) (50,491)
		2	d	2		
P	Veratrole, Trichloro- (isomer ?)	2	d	2	Standard C	(42,251) (50,491)
	Xylene, Dichloro-	2	d	1	Standard A	NONE(?)
		2	a	1		
	Xylene, Trichloro- or (trichloroethyl benzene ?)	2	b	2	8 Pk Index	(50,36)
		2	d	1		
		2	a	1		

APPENDIX B

UNIDENTIFIED COMPOUNDS CHARACTERIZED BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Available mass spectra of these compounds appear in Appendix F

COMPOUND	DISCHARGER	LOCATION	EXTRACT	LITERATURE (Ref. No.,page)
Unidentified Resin Acid, [methyl ester derivative] (MW 316)	2	d	4	
Unidentified Resin Acid, [methyl ester derivative] (MW 318)	2	d	4	
Unidentified Resin Acid, [methyl ester derivative] (MW 328) (2 isomers)	2	d	4	
Unidentified Chloro Resin Acid, [methyl ester derivative] (MW 362)·	2	d	4	
Either $C_{14}H_{12}O$ or $C_{15}H_{16}$ compound with an apparent molecular weight of 196, 2 isomers	2	a	1	(45,27)
	2	d	1	(40,204)
	2	a	1	
	2	a	1	
	16	d	1	
		2 carp	1	
	25	a	1	
		carp	2	
	1	b	2	
	2	b	2	
	2	a	2	
	2	d	2	
	2	d	3	
	1	d	3	
	12	a	3	
	12	d	3	
Monochloro compound with an apparent molecular weight of 230 -- probably above chlorinated (several isomers)	2	a	1	
	2	d	1	
	2	a	1	
	2	a	1	
	2	a	1	
		2 carp	1	
	2	b	2	

COMPOUND	DISCHARGER	LOCATION	EXTRACT	LITERATURE (Ref. No.,page)
Dichloro compound with an apparent molecular weight of 264 -- probably unknown MW 196 compound chlorinated (several isomers)	2	d	1	
	2	a	1	
	2	a	1	
	2	a	1	
	2	a	1	
		carp	1	
Trichloro compound with an apparent molecular weight of 298 -- probably unknown MW 196 compound chlorinated (several isomers)	2	d	1	
	2	a	1	
	2	a	1	
	2	a	1	
	2	a	1	
Nonhalogenated, with an apparent molecular weight of 238	2	a	1	
	2	b	2	
	2	d	3	
		carp	2	
Monochloro compound with an apparent molecular weight of 272 -- probably unknown MW 238 chlorinated	2	a	1	
Dichloro compound with an apparent molecular weight of 306	2	a	1	
	2	a	1	
Nonhalogenated compound with an apparent molecular weight of 272 -- diterpene related	2	a	2	(22)
	17	d	1	
		carp	1	
Nonhalogenated compounds with an apparent molecular weight of 286 -- apparently diterpene alcohols (up to 7 isomers)		2 carp	1	(27-28)
		carp	2	
	2	a	2	(30)
	2	d	2	
	2	d	3	
	12	d	3	
Monochloro compound with an apparent molecular weight of 320	2	d	2	
Monochloro compound with 339-41 ion cluster	24	c	2	
Monochloro compound with 168-70 ion cluster	25	a	1	
Monochloro compound with 230-2 ion cluster	25	a	3	

COMPOUND	DISCHARGER	LOCATION	EXTRACT	LITERATURE (Ref. No.,page)
Monochloro compound with 244-6 ion cluster	25	a	3	
Dichloro compound with 193-7 ion cluster	25	a	3	
Dichloro compound with 202-6 ion cluster	2	d	3	

APPENDIX C

RELATIVE RETENTION TIME INDEX OF COMPOUNDS/DERIVATIVES IN ACID EXTRACTS

Though similar in polarity to the common higher-loaded Carbowax 20M column packings, the low-loaded, thermally treated, and deactivated Ultra-Bond 20M column packing has not been extensively used in environmental analysis. The reports of Aue (37) and Karasek and Hill (38) provide the basis for the recent commercialization of this column packing. Because of our unfamiliarity with the elution characteristics of this packing, Appendix C provides a tabulated retention time index relative to aldrin for eluting times of compounds or derivatives extracted from the acidic fraction. This column packing resolved pentachloroanisole from tetrachloroveratrole, which was not possible with 3% OV-17, 6% SP-2401/4% SE-30, or 3% SP-2100 column packings.

APPENDIX C

Relative Retention Time Index of Compounds/Derivatives in Acid Extracts

GLC Column: 3 m x 2mm i.d. Ultra-Bond 20M 100/120 mesh, temperature programmed 110-250°C at 4°/min, helium flow ca. 15-20 mL/min

$$\text{Relative retention time index} = \frac{\text{retention time of compound}}{\text{retention time of aldrin}}$$

Retention time of aldrin *ca*. 14 minutes

Compound/Derivative	RRT Index	MW	Significant ions "_" Ion(s) searched by LMRGC
Chloroanisole-(isomer?)	0.12	142	142
Methyl benzoate	0.13	136	136
Tetrachloroacetone	0.15	194	83, 85
Methyl salicylate	0.20	152	92, 120
Trichloroanisole-(2,4,6)	0.21	210	195, 197, 210, 212, 167, 169
Guaiacol	0.22	124	109, 124, 81
Benzyl alcohol	0.23	108	79, 108
Dichloroanisole-(isomer?)	0.26	176	133, 135, 161, 168, 176, 178
Benzothiazole	0.27	135	135, 108
Phenol	0.31	94	94
Dimethylbenzoate	0.38	150	119, 91, 117, 150
Tetrachloroanisole-(isomer?)	0.42	244	244, 246, 248, 201, 203, 205
Dichlorophenol-(isomer?)	0.42	162	162, 164
Methyl methoxybenzoate	0.44	166	135, 166
Dichlorophenol-(isomer?)	0.51	162	162, 164, 63, 98
Ethyl phenol	0.53	124	107, 122
Nonyl anisole-(isomer?)	0.55	234	149, 121
Nonyl anisole-(isomer?)	0.57	234	121, 163
Trichlorophenol-(2,4,6)	0.66	196	97, 99, 196, 198
Pentachloroanisole	0.68	278	278, 280, 282, 284
Tetrachloroveratrole	0.73	274	259, 261, 263, 274, 276, 278
Methyl thiobenzothiazole	0.74	181	148, 181, 108
Trichloroveratrole-(isomer?)	0.76	240	225, 227, 240, 242
Benzoic acid	0.78	122	105, 122, 77
Trichloro-trimethoxybenzene	0.79	270	270, 272, 274

Dichloroguaiacol-(isomer?)	0.87	206	192, 194
Methoxybenzothiazole	0.89	165	136, 165
Trichlorophenol-(2,4,5 or 2,3,4)	0.90	196	97, 99, 196, 198
Vanillin	0.93	152	151, 152
Dichloroguaiacol-(isomer?)	0.97	192	177, 179, 149, 151, 192, 194
Methyl palmitate	0.98	270	74, 87 ... 270
ALDRIN (External Standard)	1.00	362	66, 261, 263, 265
Acetovanillone	1.03	166	151, 166
Tetrachlorophenol-(2,3,4,6 or 2,3,5,6)	1.06	230	230, 232, 234, 236
Trichloroguaiacol-(isomer?)	1.08	226	226, 228, 230
Methyl heptadecanoate	1.13	284	74, 87, ... 284
Lauric Acid	1.16	200	73, 60, ... 200
Methyl oleate	1.27	296	55, 74, 83, ... 296
Trichloroguaiacol-(isomer?)	1.27	226	211, 213, 226, 228
Methyl stearate	1.30	298	74, 87, ... 298
Trichloroguaiacol-(4,5,6)	1.34	226	226, 228, 230
8,15 Isopimardiene-18-oate	1.36	316	91, 105, 241, 316
Syringaldehyde	1.38	182	182, 181, 65, 93, 96, 111
Myristic acid	1.40	228	73, 60, 129, ... 228
Methyl pimarate	1.41	316	121, 180, 241, 301, 316
Methyl sandaracopimarate	1.44	316	121, 301, 316
Tetrachloroguaiacol	1.45	260	260, 262, 264
Bisphenol A-dimethyl ether derivative	1.48	256	241, 256
Pentachlorophenol	1.48	264	264, 266, 268, 270, 165, 167
Unidentified Resin Acid Methyl Ester (RAME)	1.53	316	91, 105, 119, ... 241, 257, 301, 316
Chlorosyringaldehyde	1.54	216	216, 215, 218, 127, 130
Caffeine	1.60	194	109, 194
Unidentified RAME	1.64	328	253, 313, 328
Methyl dehydroabietate	1.65	314	239, 299, 314
Palmitic acid	1.68	256	73, 129, ... 256
6,8,11,13 Abietatetraen-18-oate	1.71	312	237, 195, 197, 312
Hydroxy-benzothiazole	1.72	151	151, 96, 123

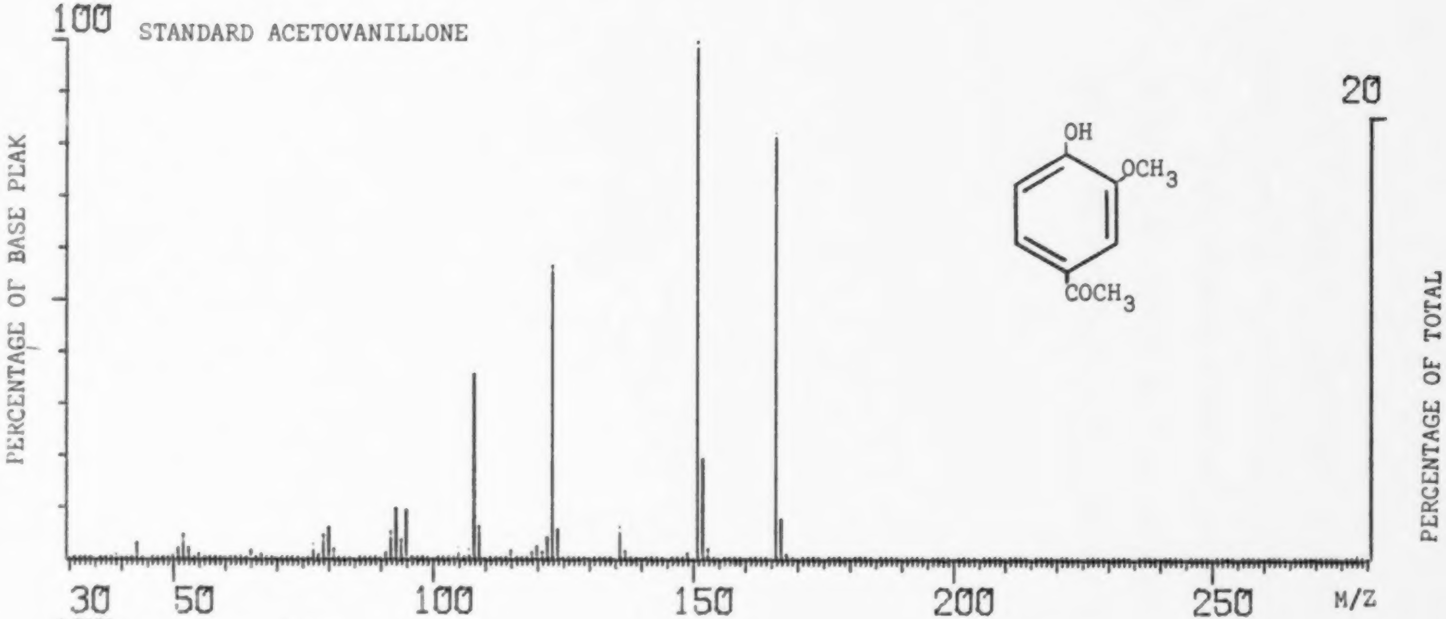
Unidentified RAME	1.76	328	253, 313, 328
Dichloro-Bisphenol A-dimethyl ether derivative (?)	1.78	324	309, 311, 313, 324, 326
Dehydroabietic acid	1.80	300	239, 285, 300
Chloro-bisphenol A-dimethyl ether derivative (?)	1.81	290	275, 277, 290, 292
Chloro-RAME	1.86	362	287, 289, 347, 349, 362, 364
Chloro-methyl dehydroabietate isomer A	1.91	348	273, 275, 333, 335, 348, 350
Stearic acid	1.93	284	55, 73, 129, ... 284
Chloro-methyl dehydroabietate isomer B	1.96	348	273, 295, 333, 335, 348, 350
Tetrachloro-Bisphenol A-dimethyl ether deriv. (?)	2.04	392	377, 379, 381, 383, 392, 394, 396
Dioctyl phthalate	2.06	390	149, 167
Trichloro-Bisphenol A-dimethyl ether derivative (?)	2.07	358	343, 345, 347, 358, 360, 362
Dichloro-Bisphenol A-dimethyl ether derivative (?)	2.10	324	309, 311, 313, 324, 326
Dichloro-methyl dehydro-abietate	2.13	382	307, 309, 311, 382, 384
Methyl oxo-dehydroabietate	2.18	328	253, 269, 296, 313, 328
Chlorinated compounds			35-36
Phthalates			149
Methyl esters of fatty acids			74+87
Resin acids (screened for)			300-302
Methyl esters of resin acids (RAME)			121, 239, 241, 253, 312, 314, 316, 318 + 328

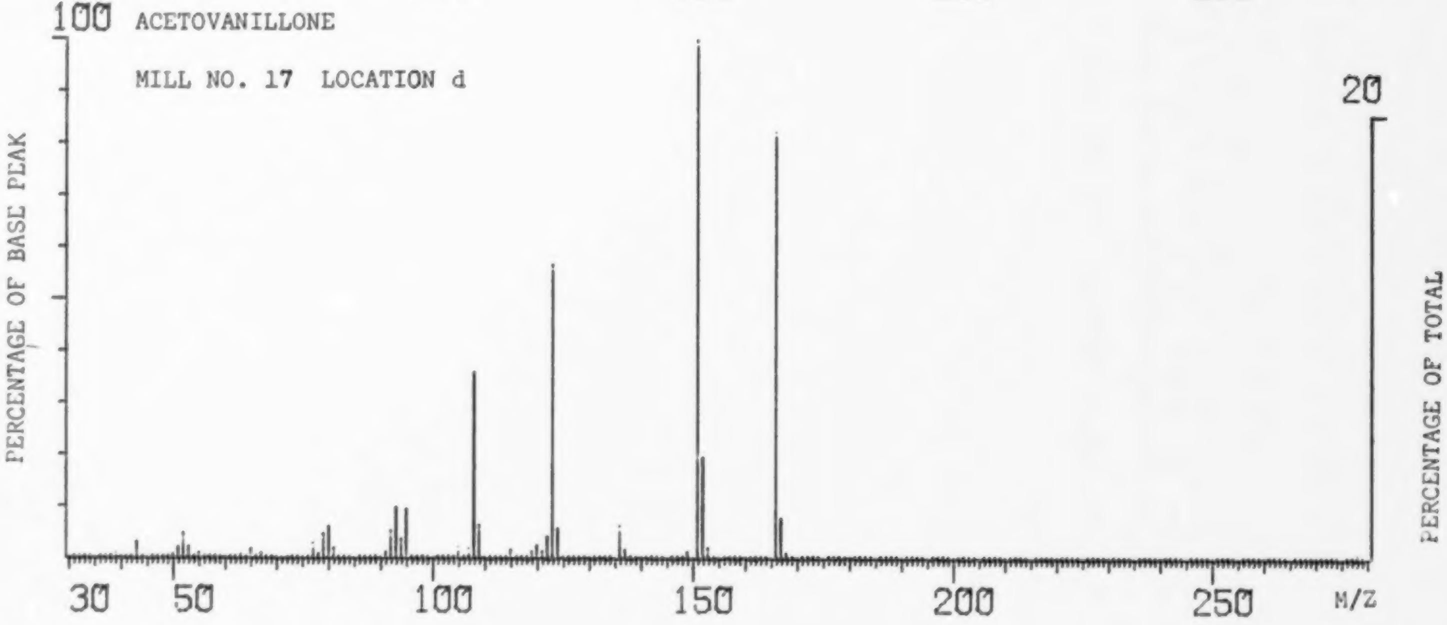
(?) - Tentative Identification

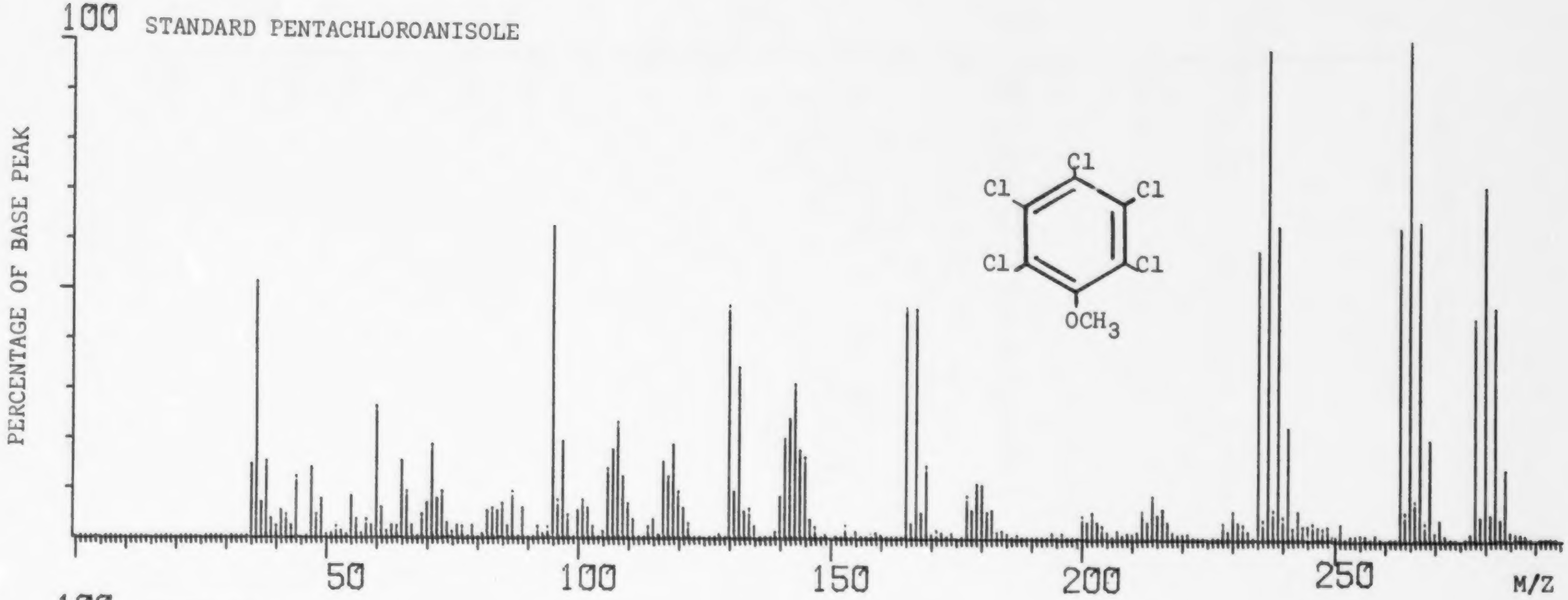
APPENDIX D

MASS SPECTRA OF SAMPLES COMPARED WITH STANDARDS

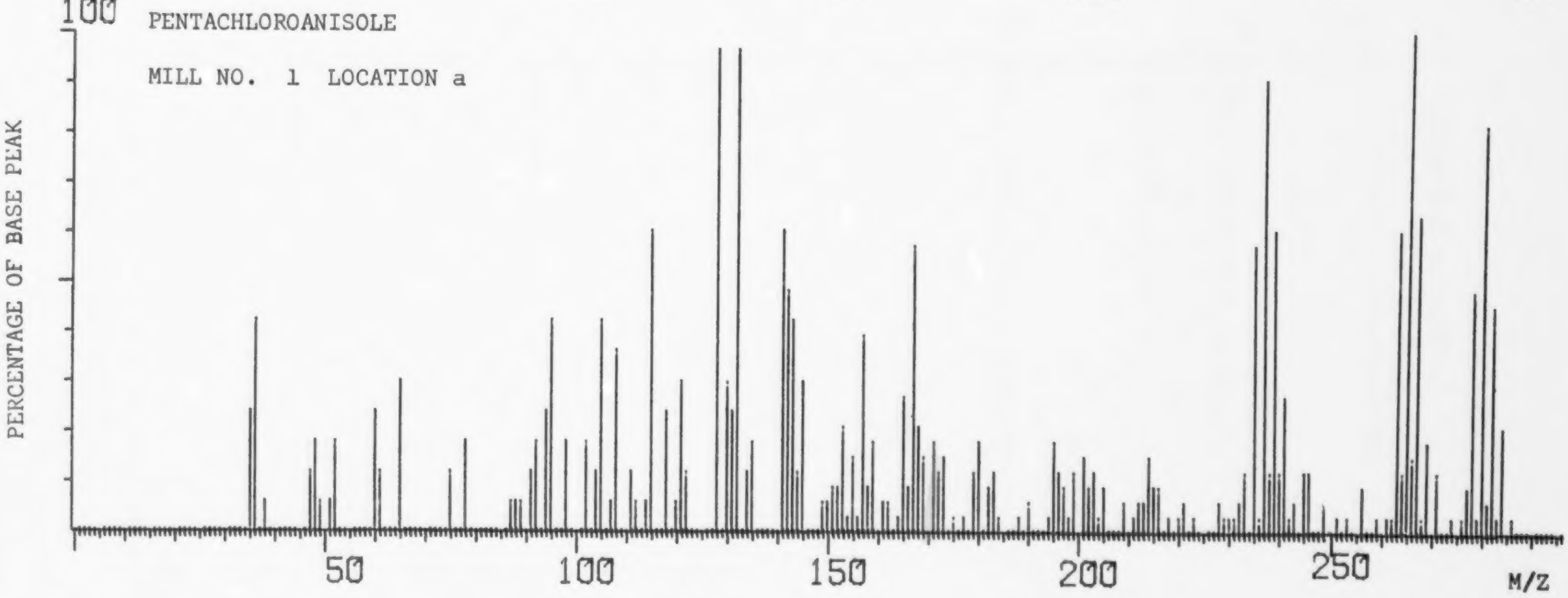
Appendix D includes many of the mass spectral comparisons of sample spectra with standard spectra. In the comparison of mass spectra of pentachloroanisole (page D-3) in Mill 1 with that of a standard, it should be noted that its presence in the sample was quantitated by GC/EC at 80 ng/L (0.08 ug/L). The amount injected into the GC/MS for the mass spectrum of this sample was ca. 8 ng.


STANDARD ACETOVANILLONE
100
PERCENTAGE OF BASE PEAK
20
PERCENTAGE OF TOTAL
OH
OCH$_3$
COCH$_3$
30
50
100
150
200
250
M/Z


ACETOVANILLONE
MILL NO. 17 LOCATION d
100
PERCENTAGE OF BASE PEAK
20
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

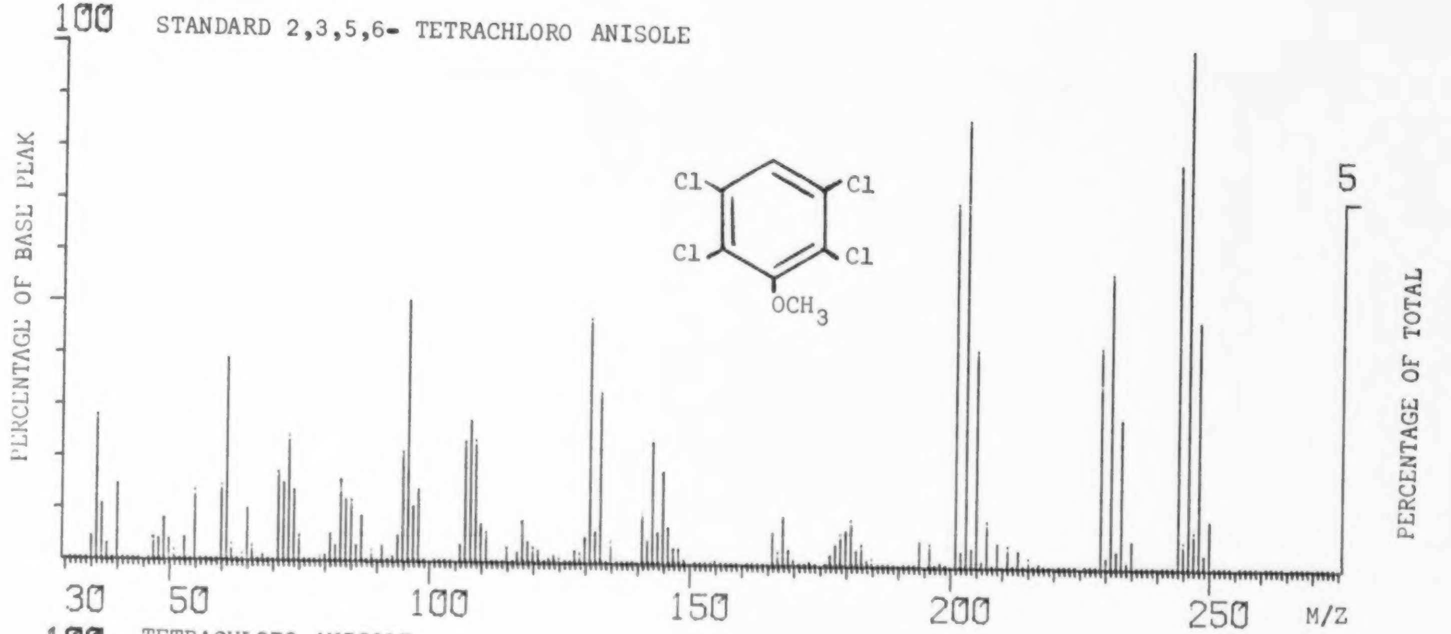


STANDARD PENTACHLOROANISOLE

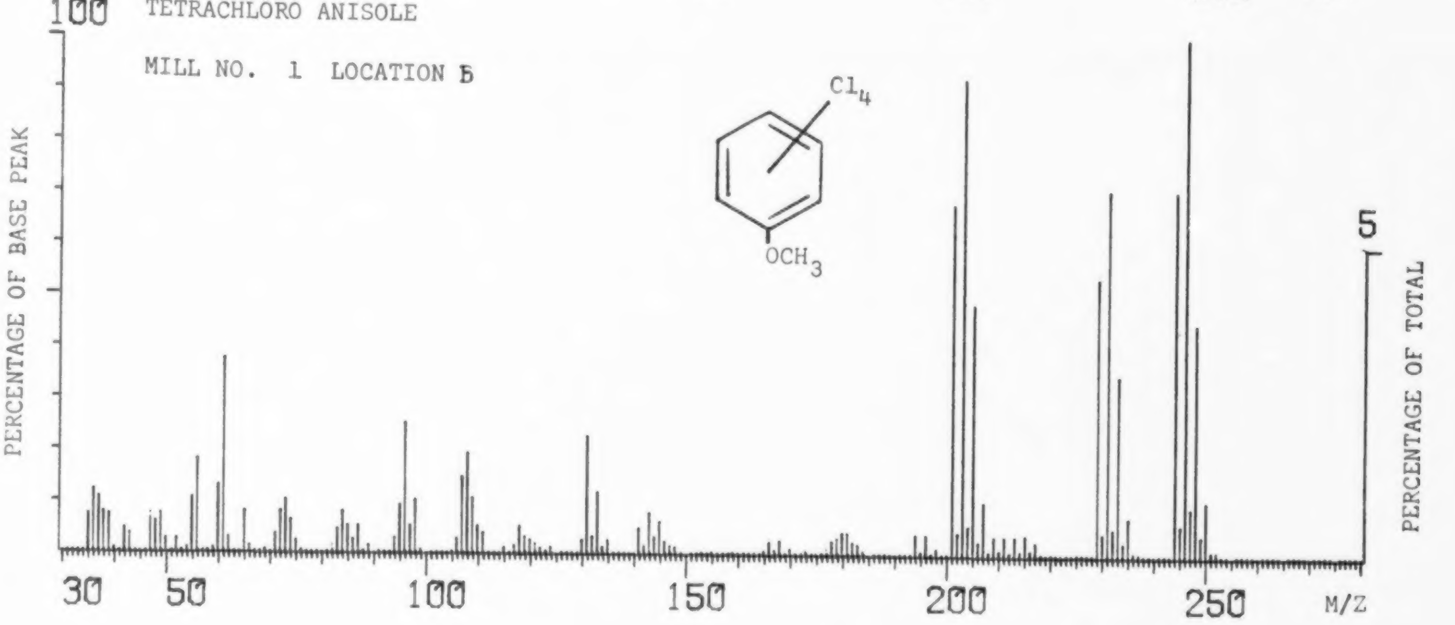


PENTACHLOROANISOLE

MILL NO. 1 LOCATION a



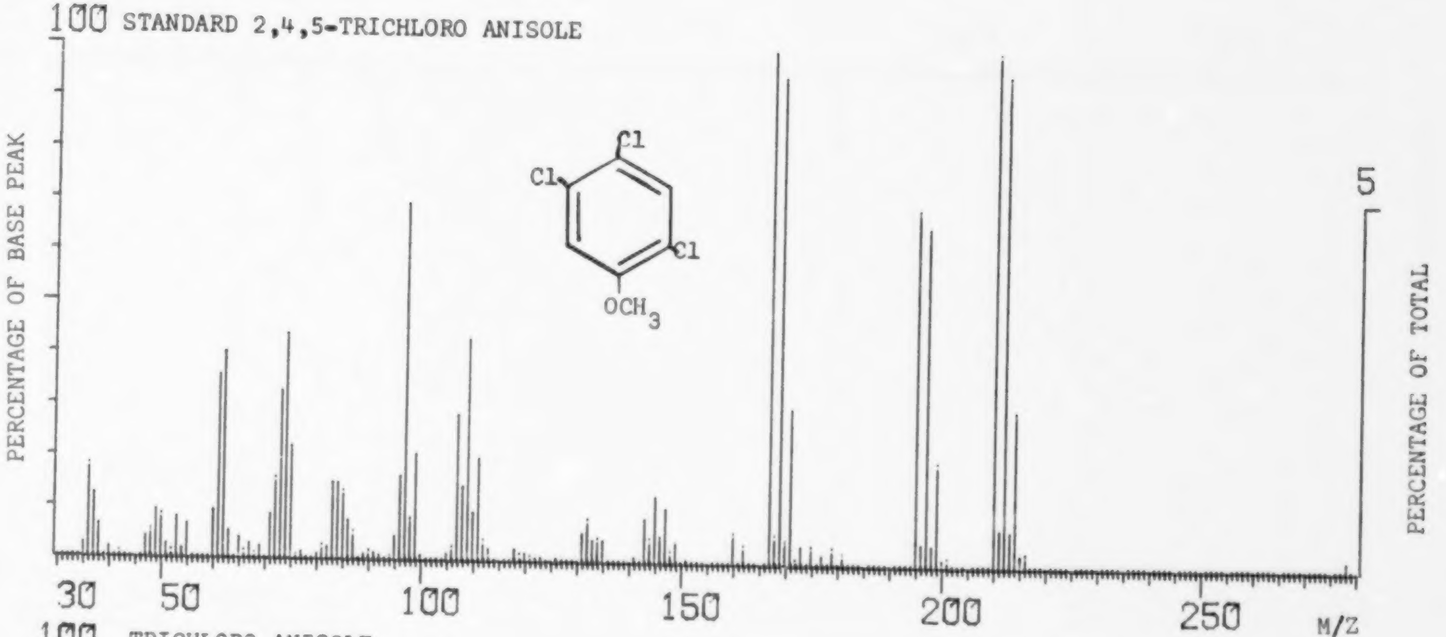
STANDARD 2,3,5,6- TETRACHLORO ANISOLE



TETRACHLORO ANISOLE

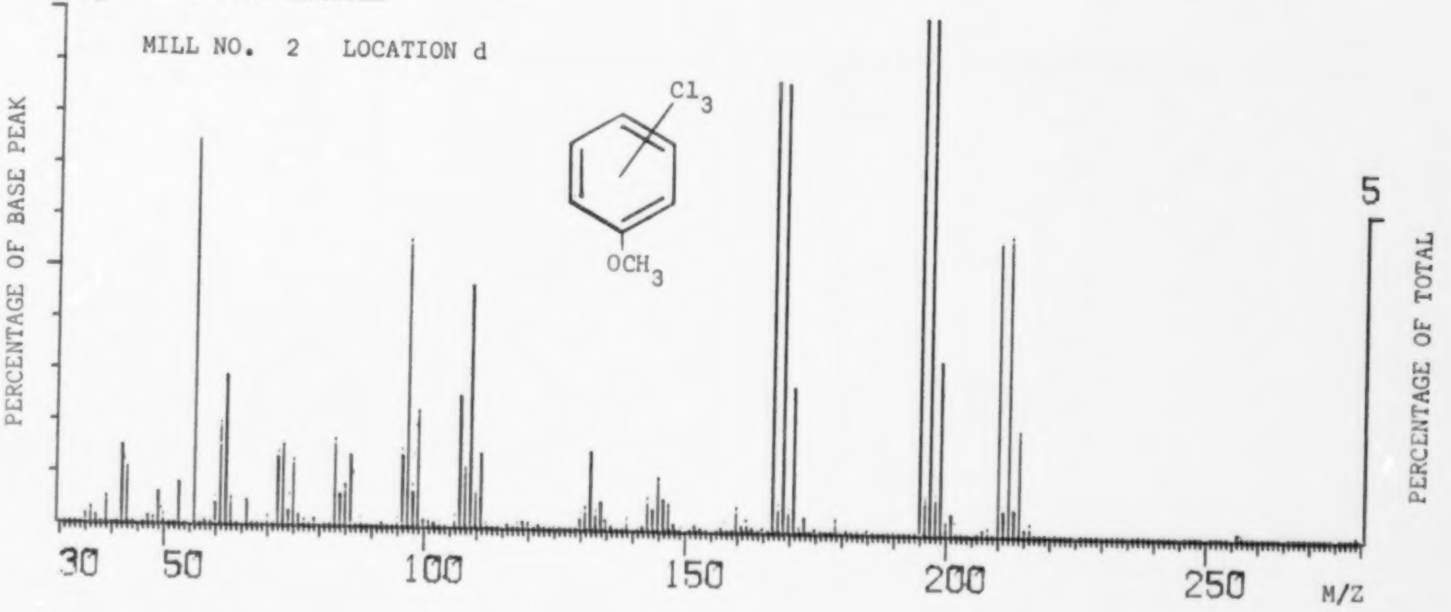
MILL NO. 1 LOCATION 5

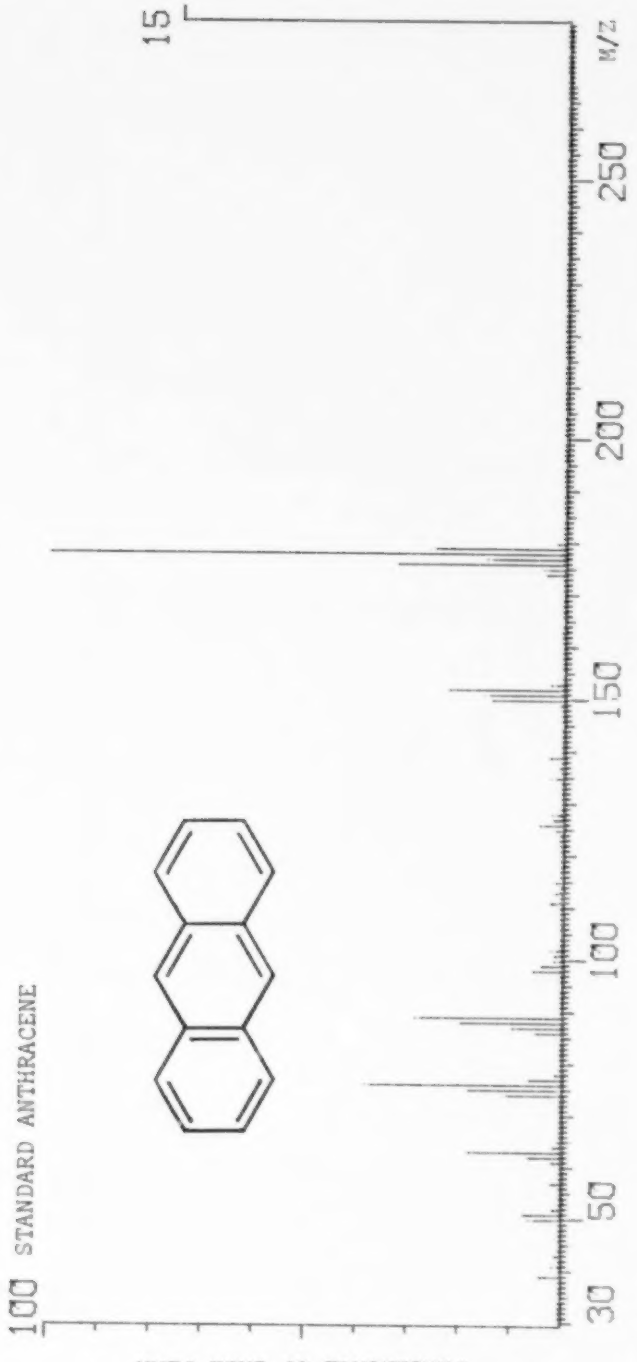
STANDARD 2,4,5-TRICHLORO ANISOLE



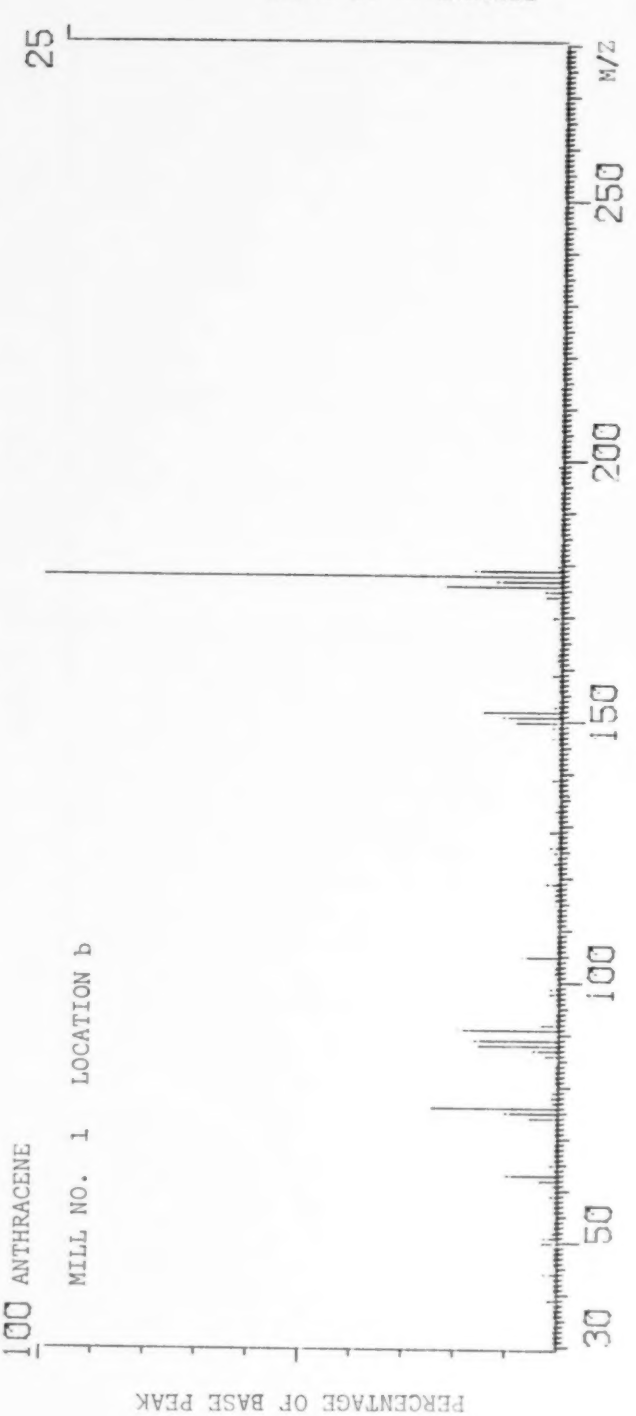
TRICHLORO ANISOLE

MILL NO. 2 LOCATION d



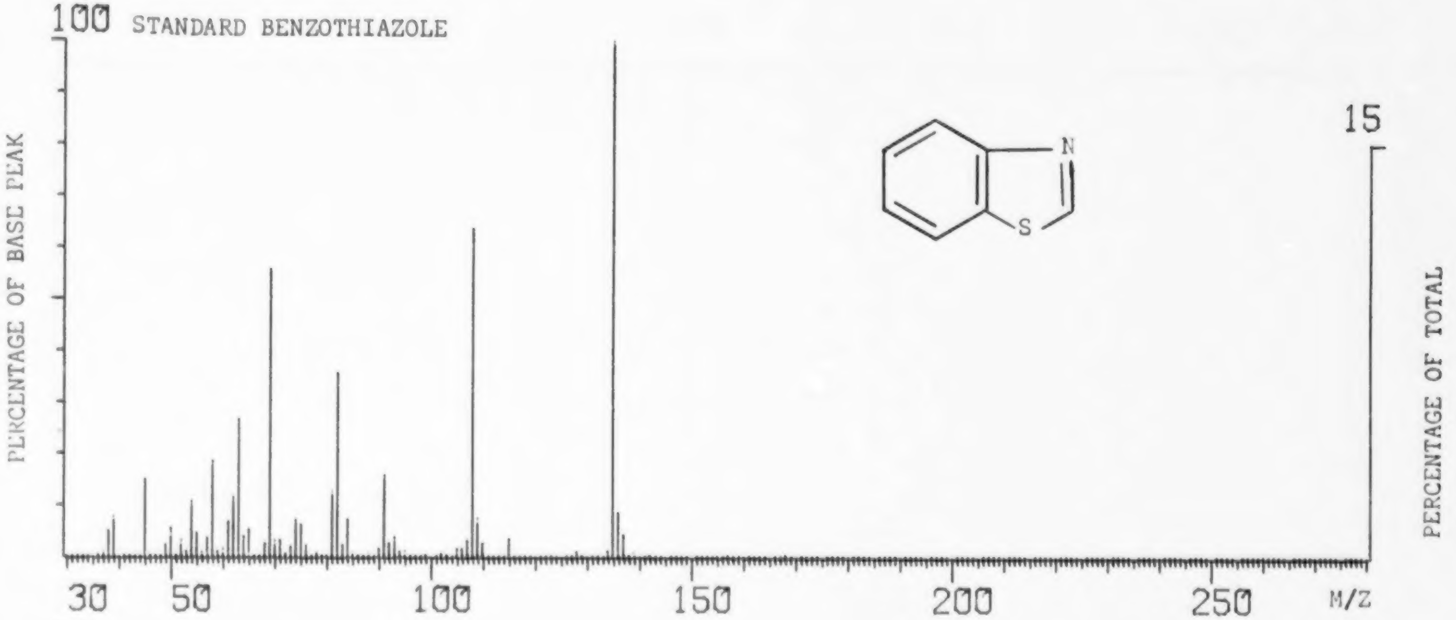


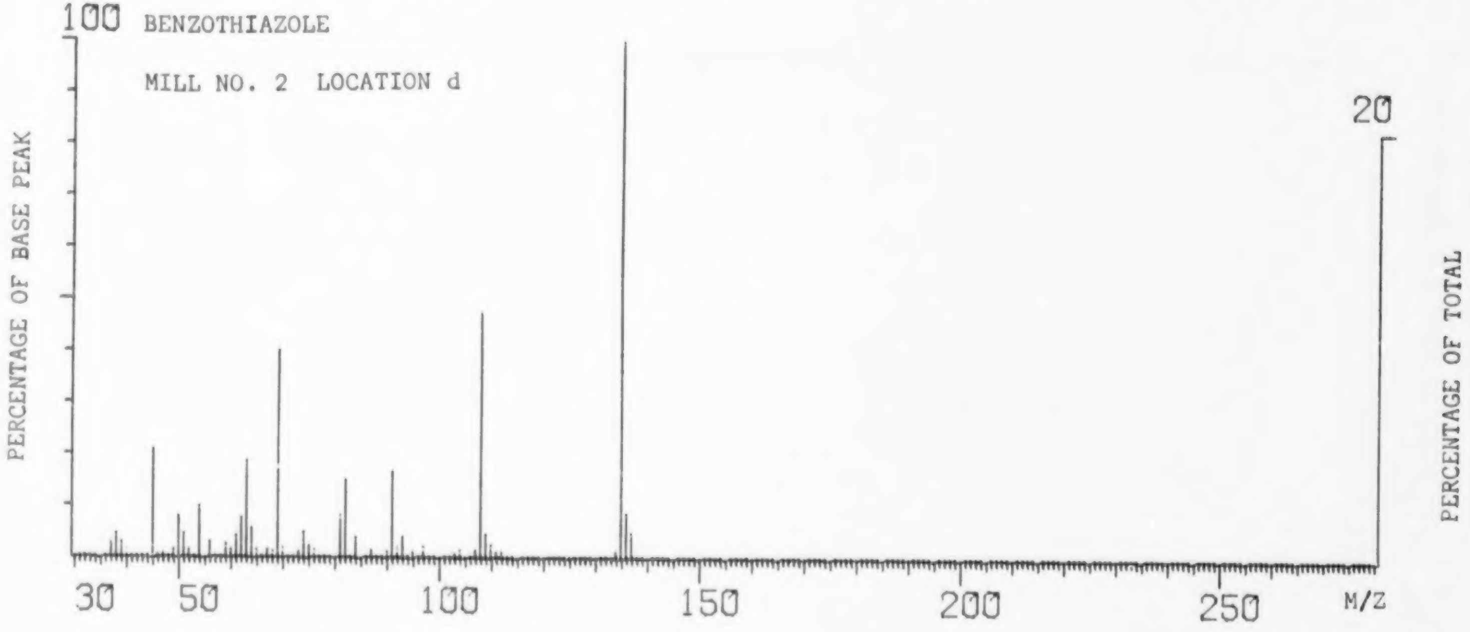
STANDARD ANTHRACENE



ANTHRACENE

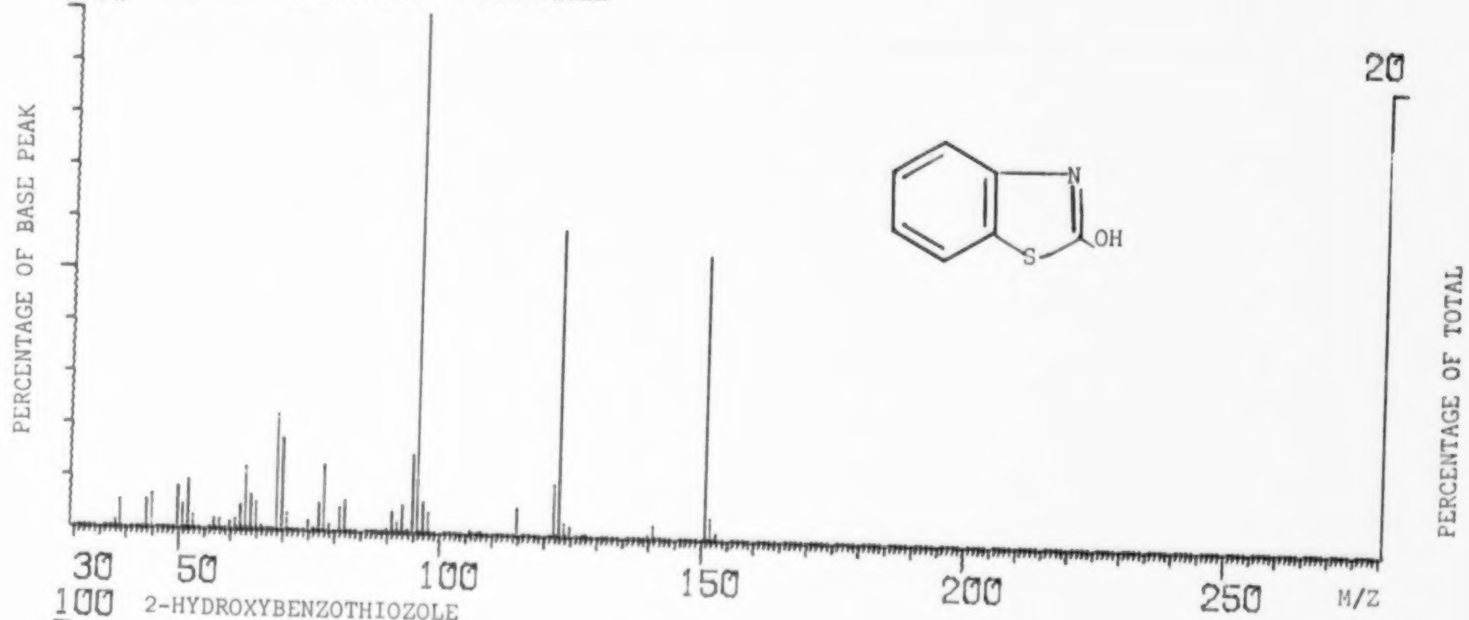
MILL NO. 1 LOCATION b


STANDARD BENZOTHIAZOLE


BENZOTHIAZOLE

MILL NO. 2 LOCATION d

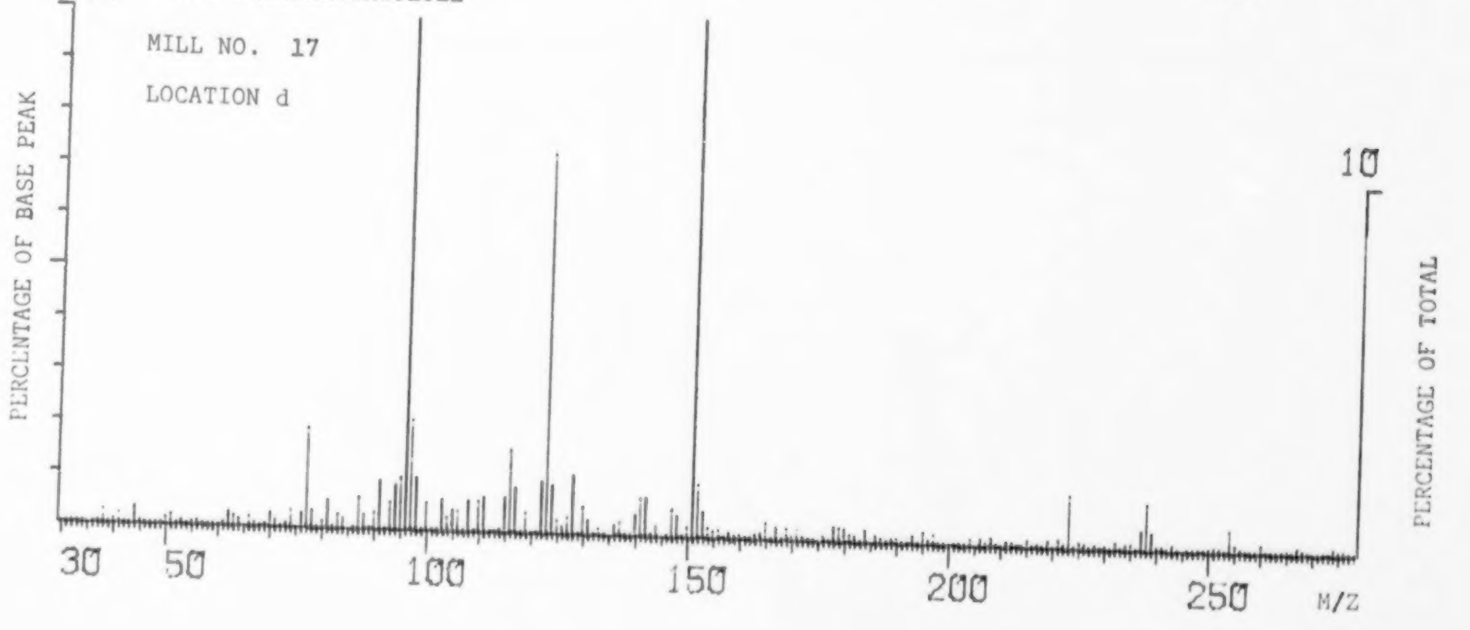
STANDARD 2-HYDROXYBENZOTHIOZOLE

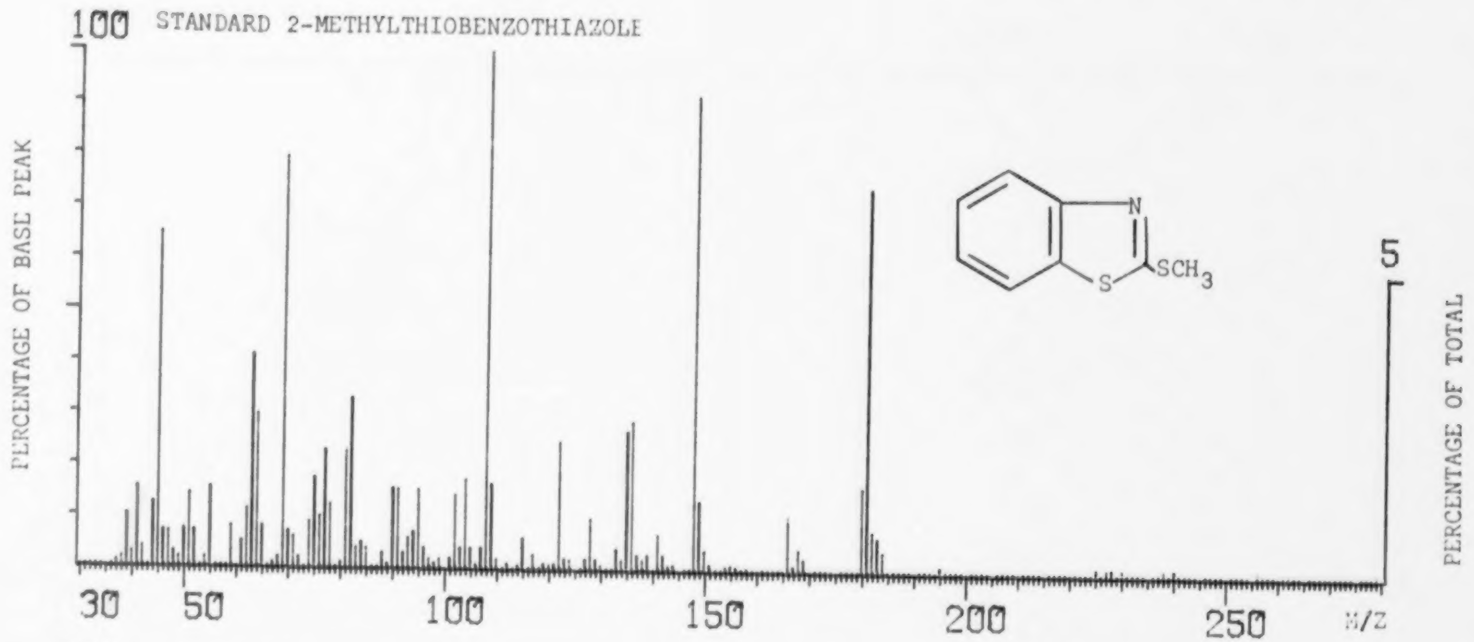


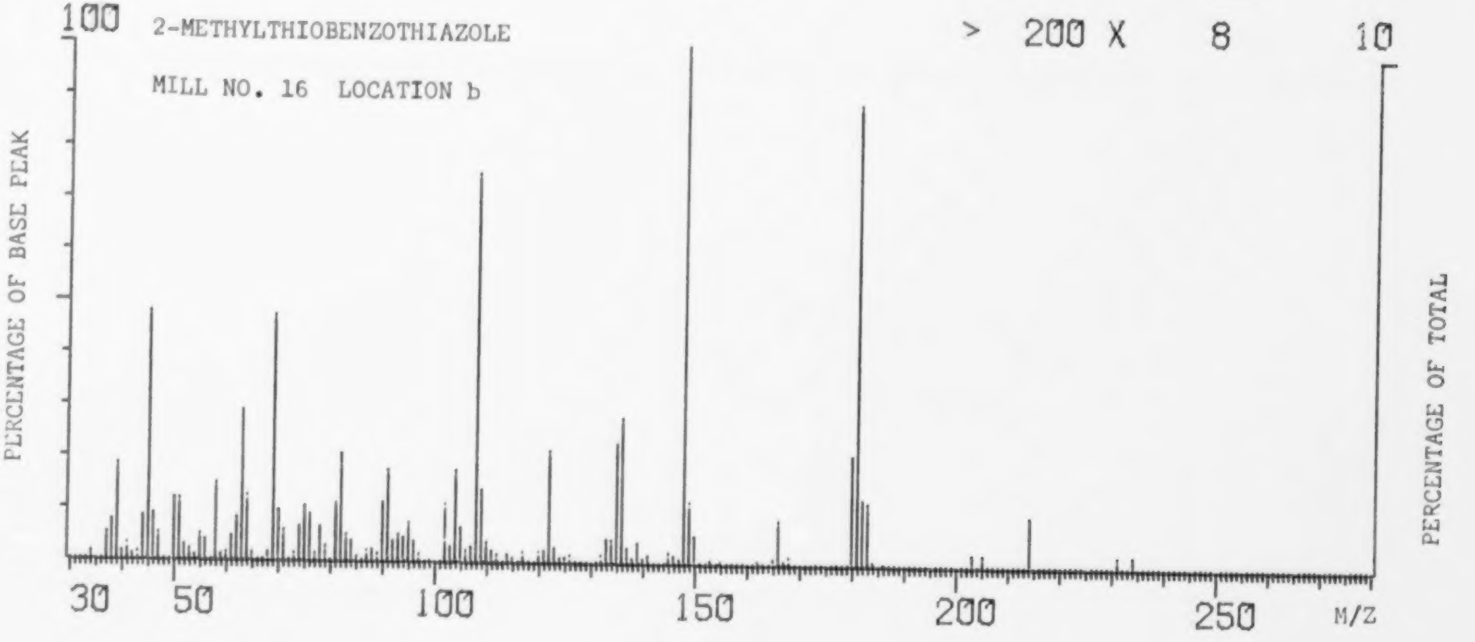
2-HYDROXYBENZOTHIOZOLE

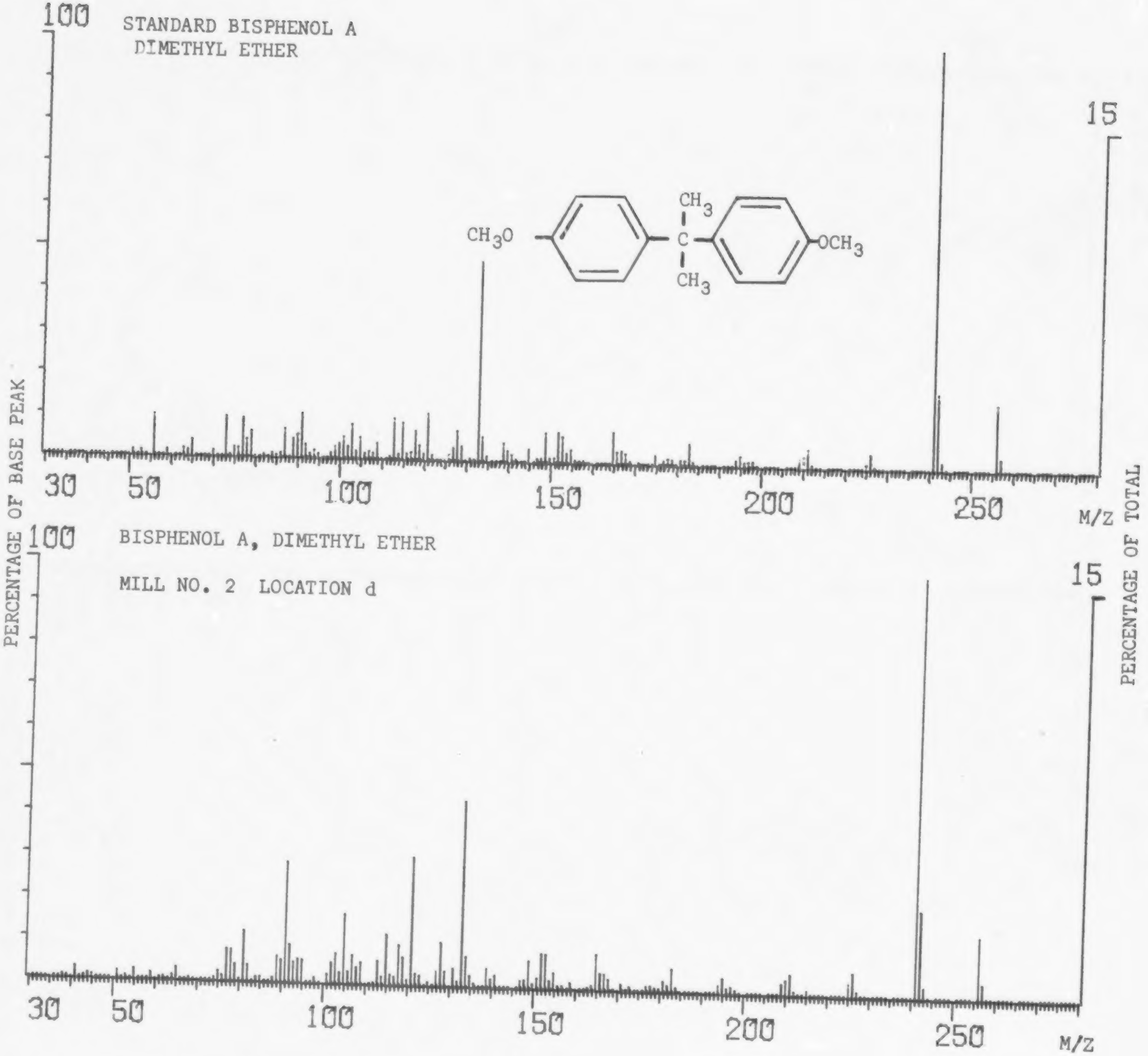
MILL NO. 17

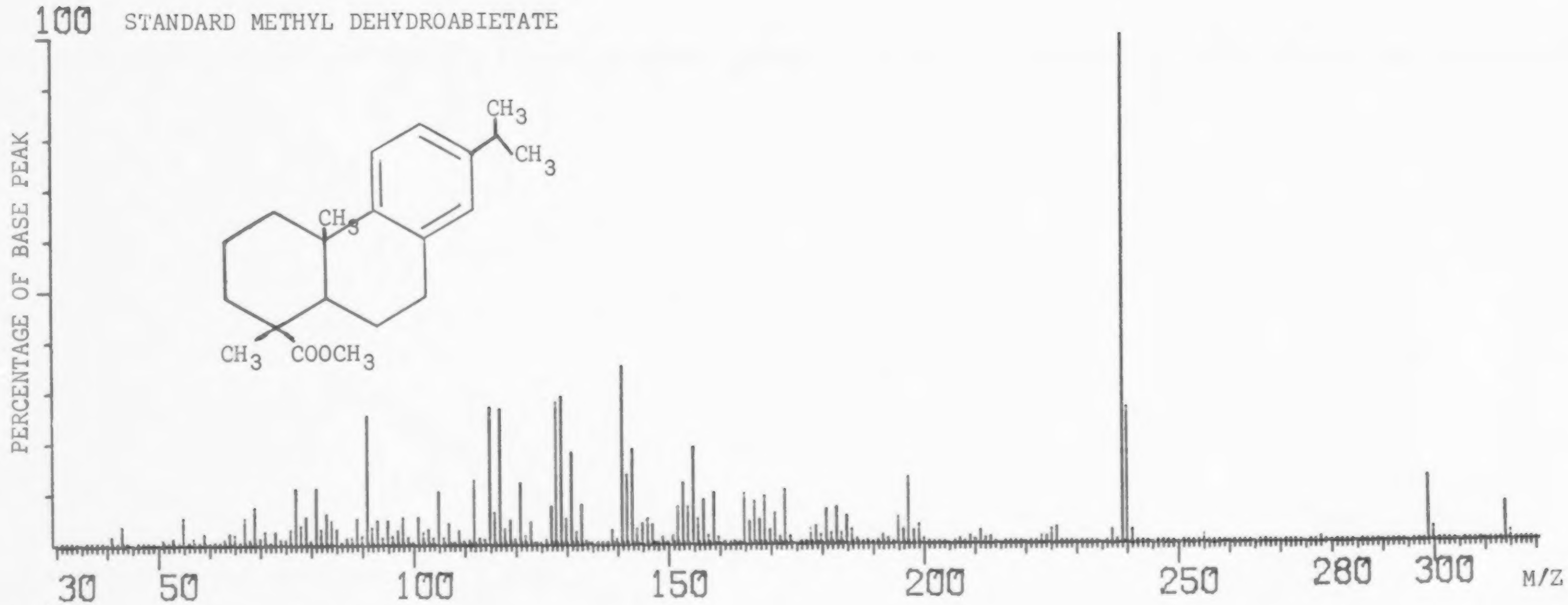
LOCATION d



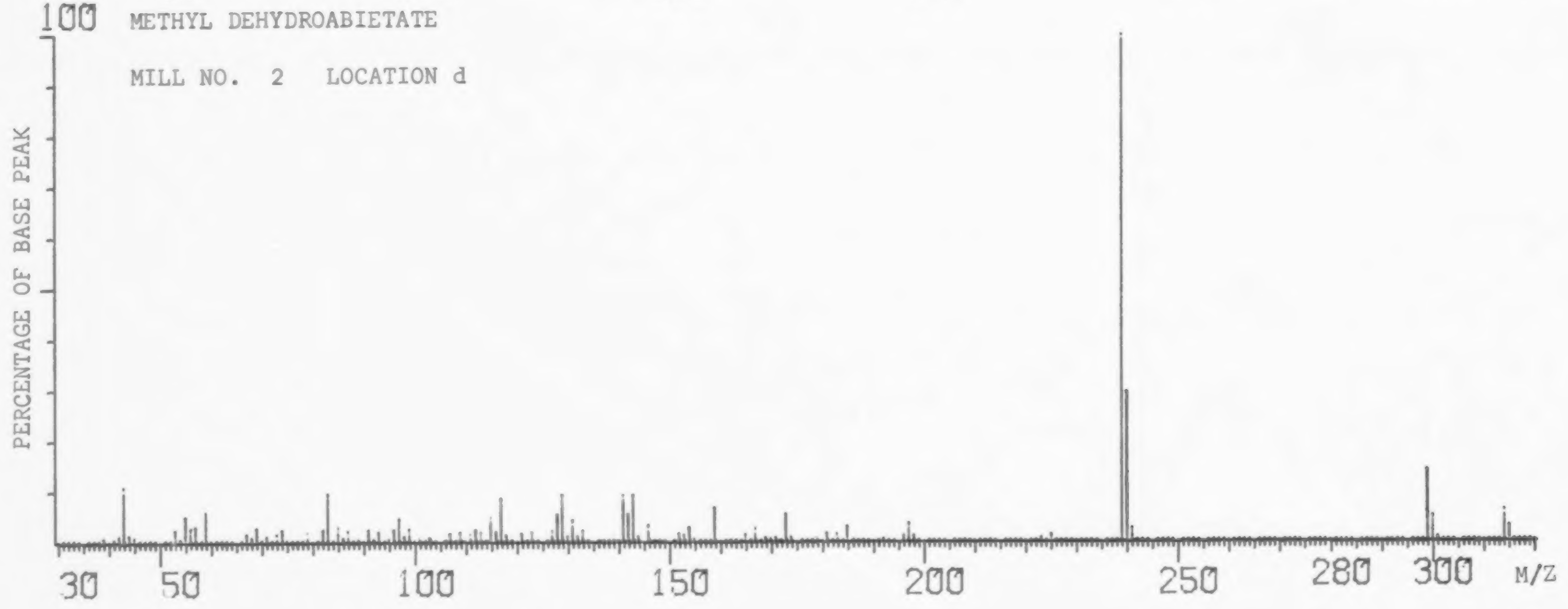

100
STANDARD 2-METHYLTHIOBENZOTHIAZOLE
N
S
SCH3
5
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


100
2-METHYLTHIOBENZOTHIAZOLE
MILL NO. 16 LOCATION b
> 200 X 8
10
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


STANDARD BISPHENOL A
DIMETHYL ETHER
CH3O
CH3
C
CH3
OCH3
100
15
30
50
100
150
200
250
M/Z
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
BISPHENOL A, DIMETHYL ETHER
MILL NO. 2 LOCATION d
100
15
30
50
100
150
200
250
M/Z

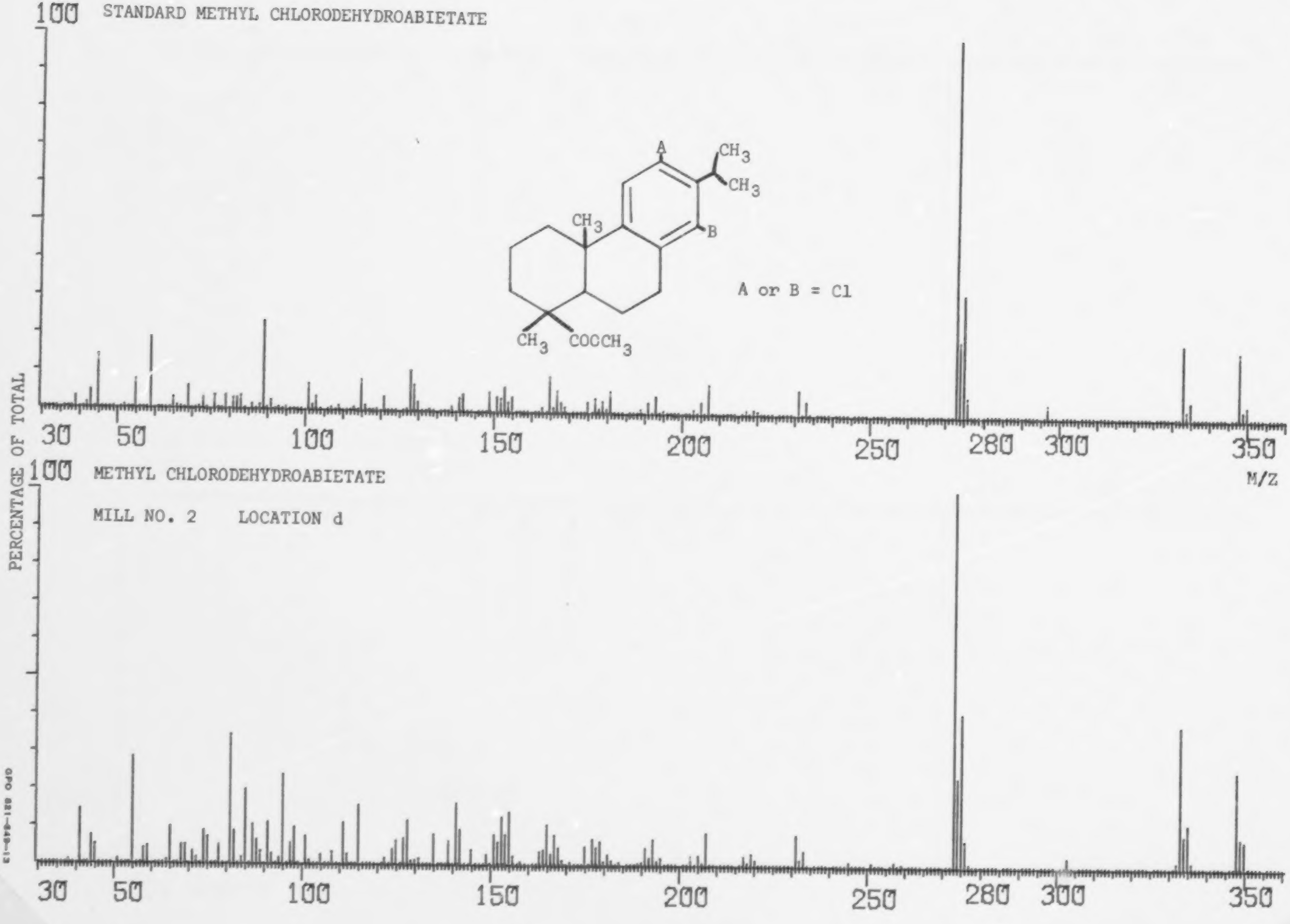


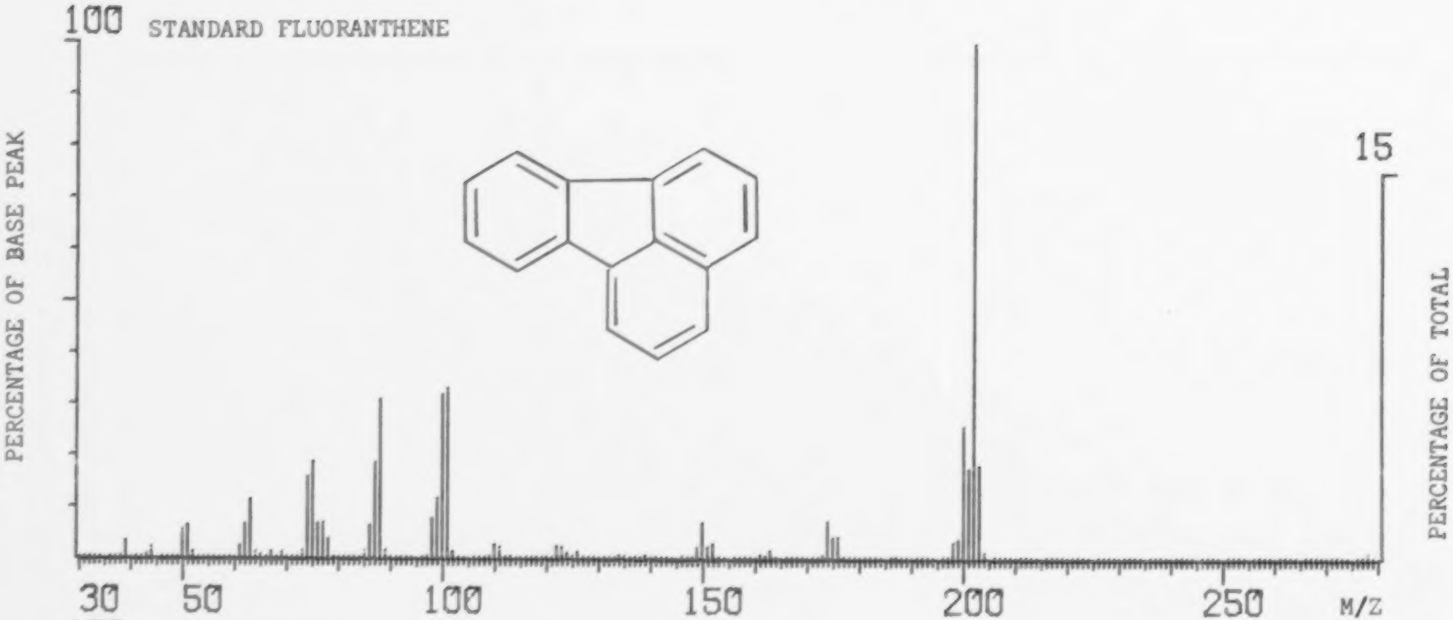
STANDARD METHYL DEHYDROABIETATE

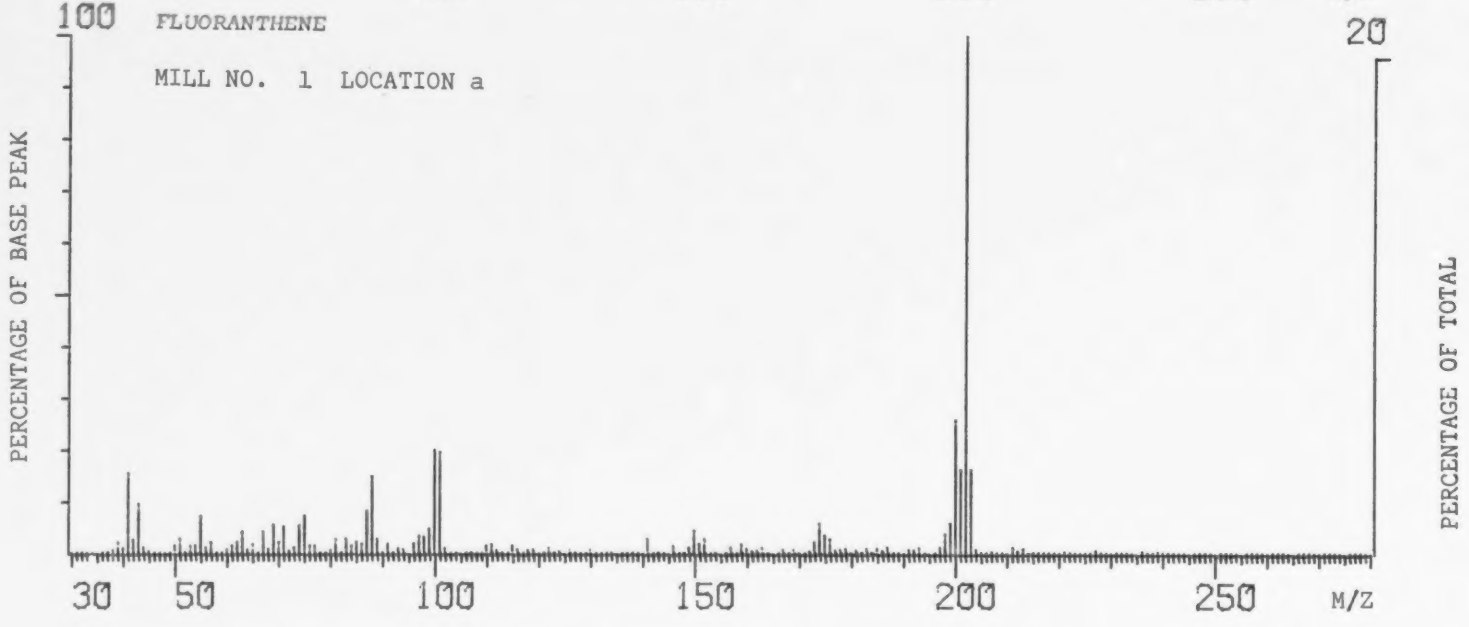


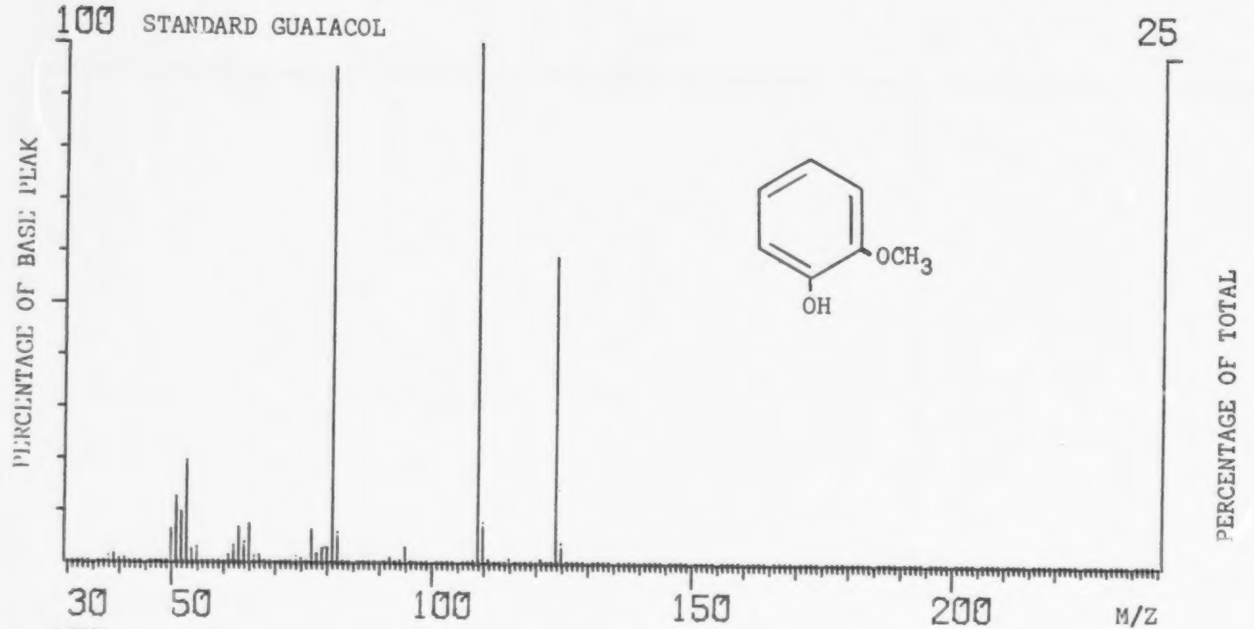
METHYL DEHYDROABIETATE

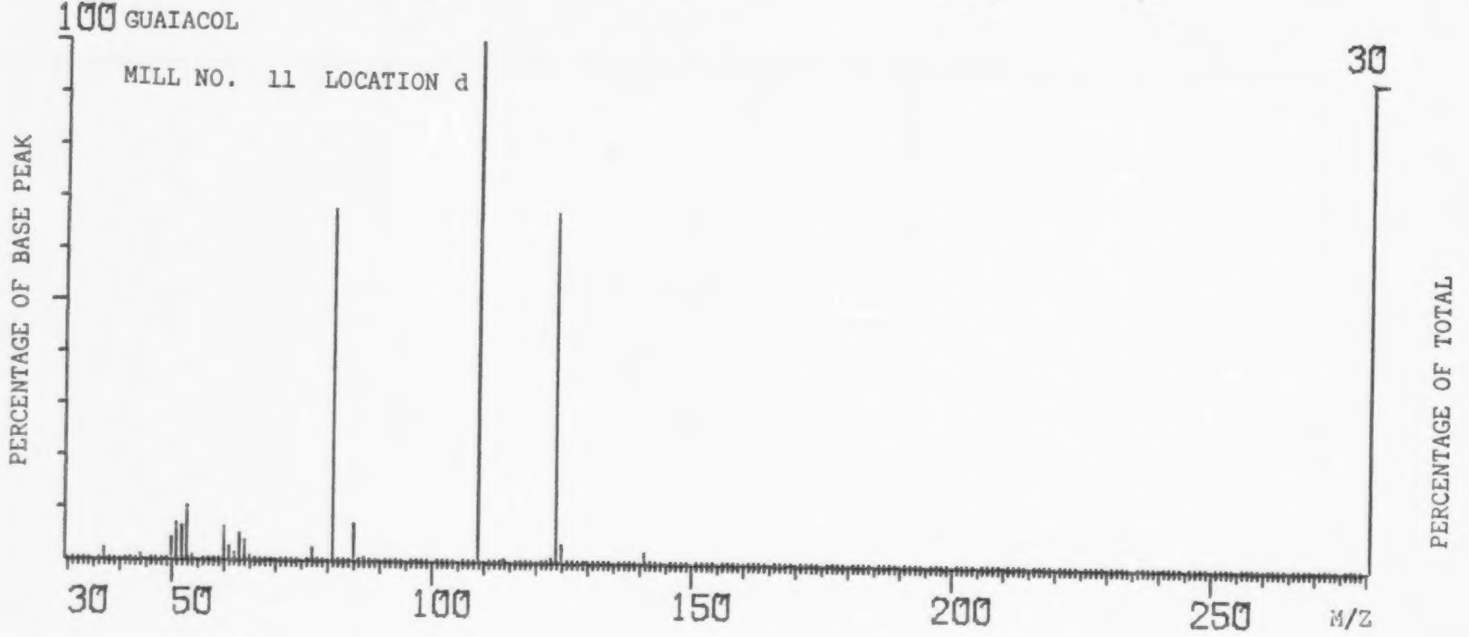
MILL NO. 2 LOCATION d

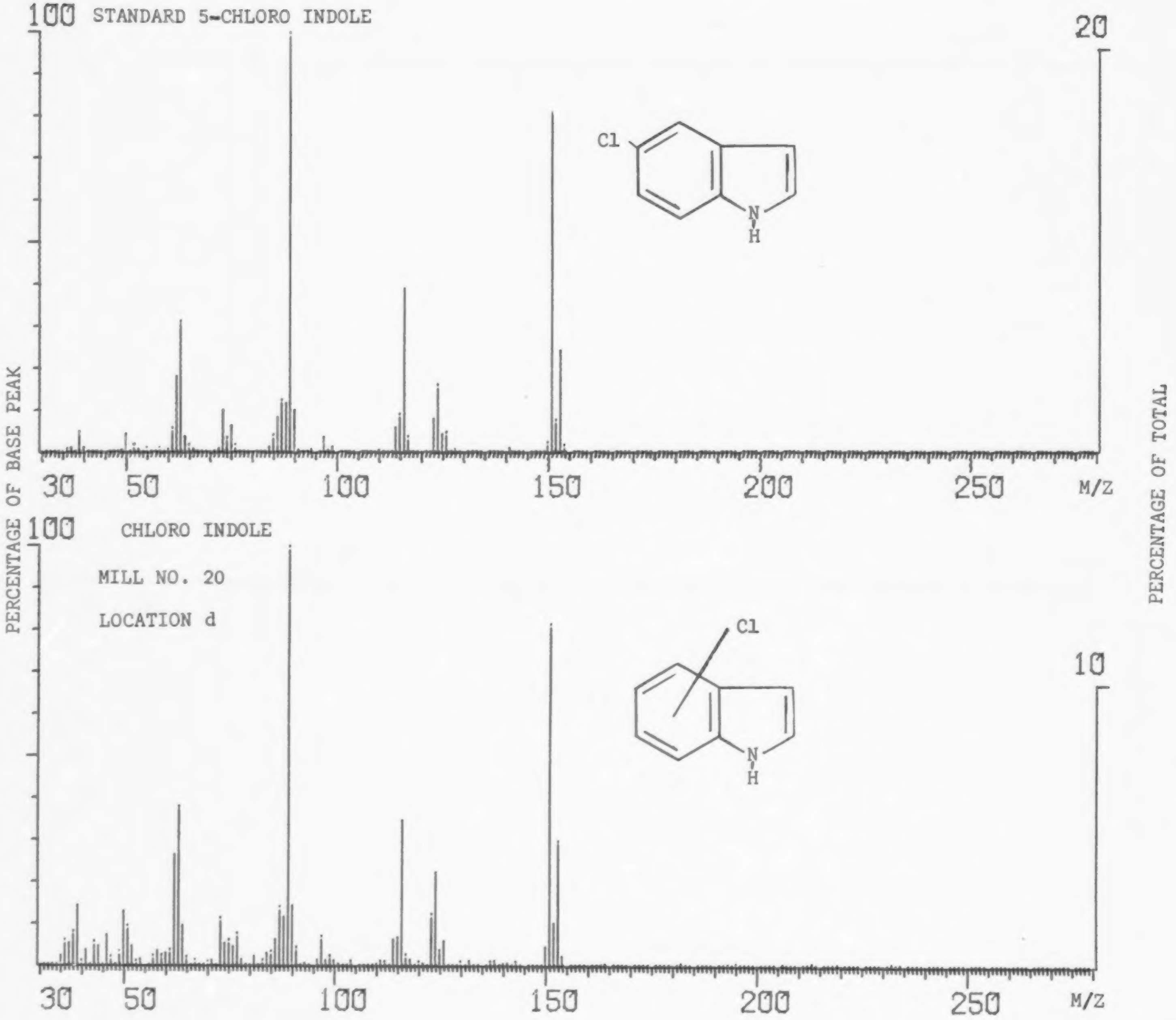

100
STANDARD METHYL CHLORODEHYDROABIETATE
CH3
CH3
CH3
A
B
CH3
COOCH3
A or B = Cl
30
50
100
150
200
250
280
300
350
M/Z
PERCENTAGE OF TOTAL
100
METHYL CHLORODEHYDROABIETATE
MILL NO. 2 LOCATION d
30
50
100
150
200
250
280
300
350

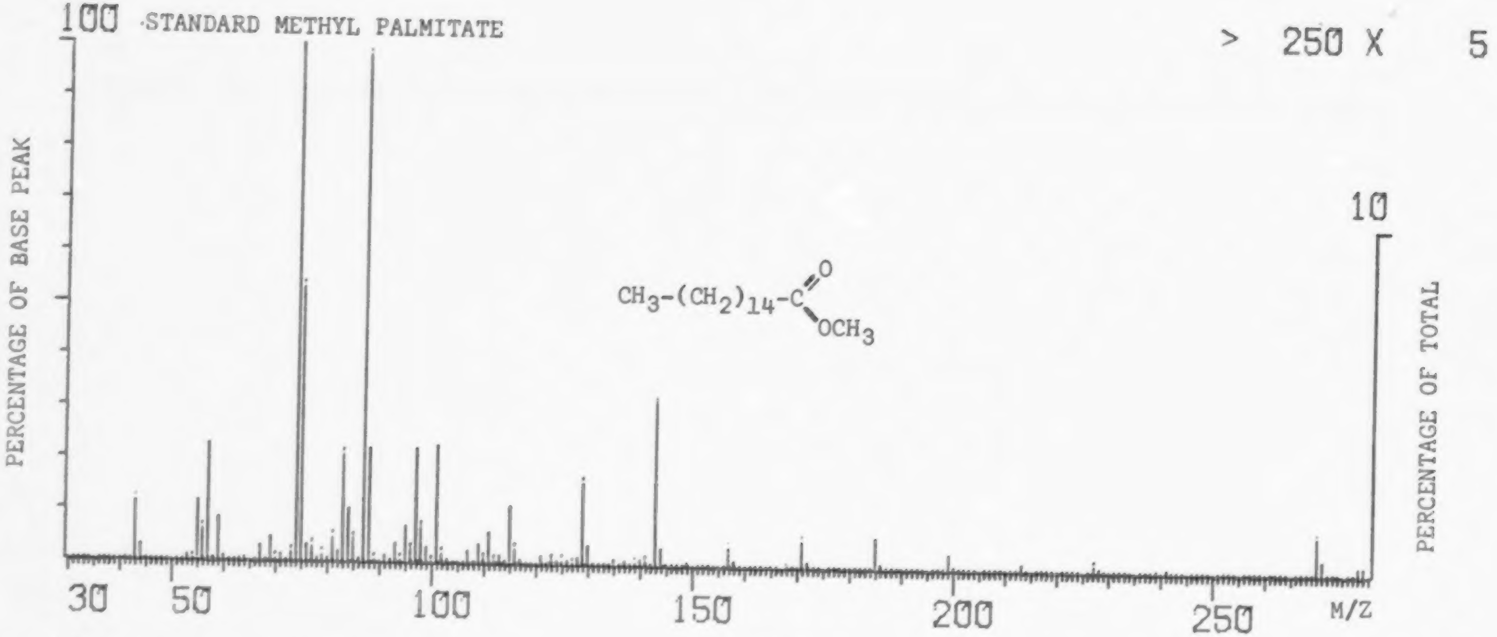

100
STANDARD FLUORANTHENE
PERCENTAGE OF BASE PEAK
15
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

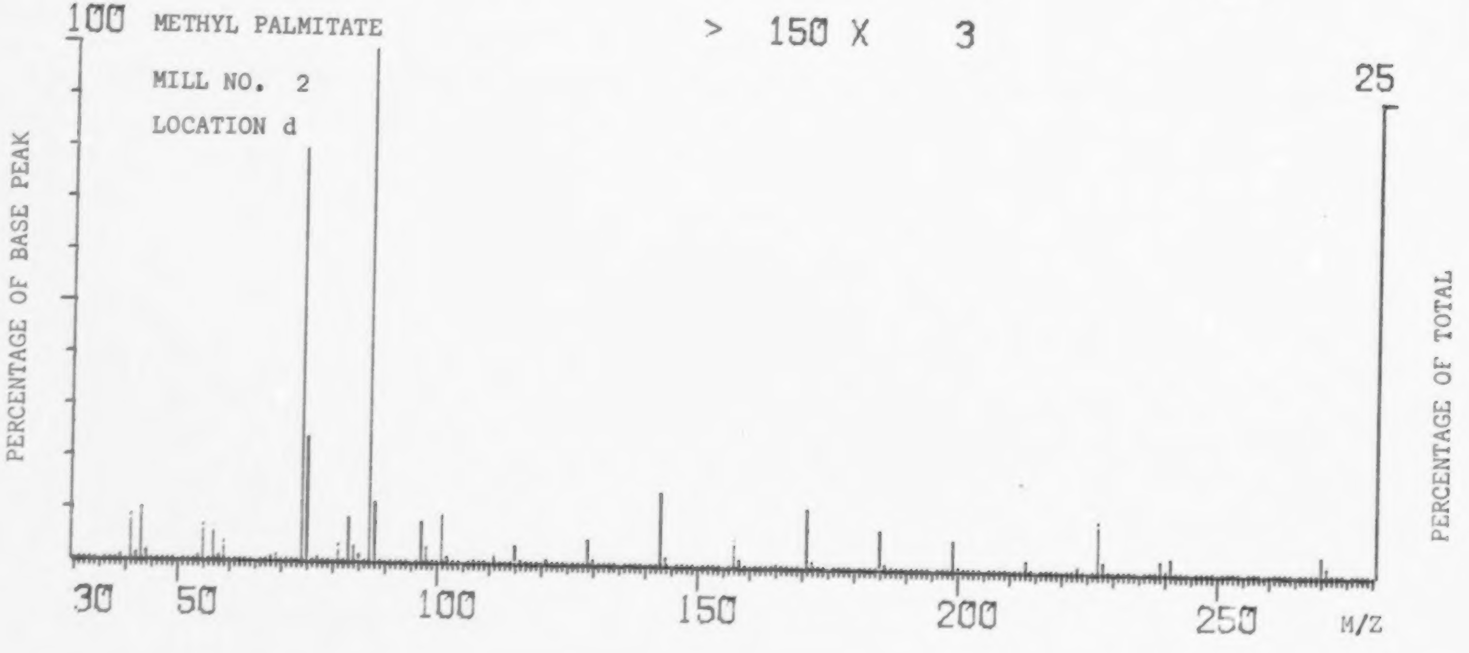

100
FLUORANTHENE
MILL NO. 1 LOCATION a
PERCENTAGE OF BASE PEAK
20
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

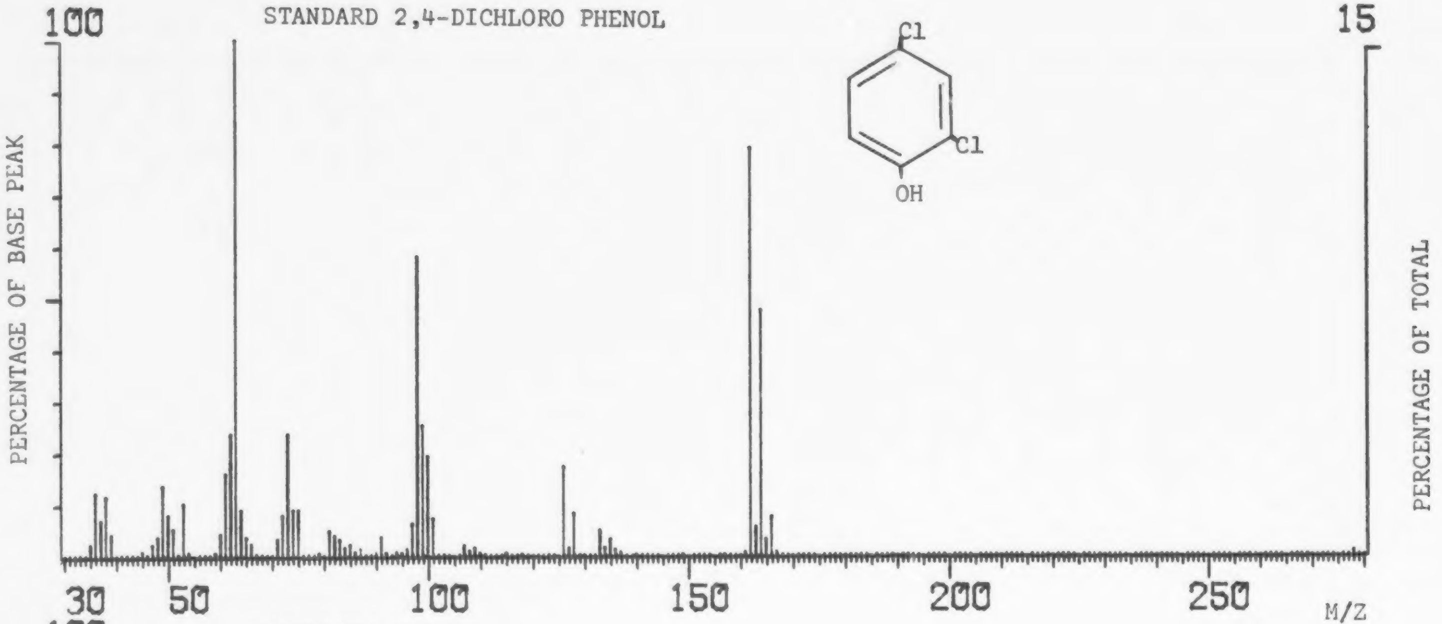

100
STANDARD GUAIACOL
25
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
OCH3
OH
30
50
100
150
200
M/Z

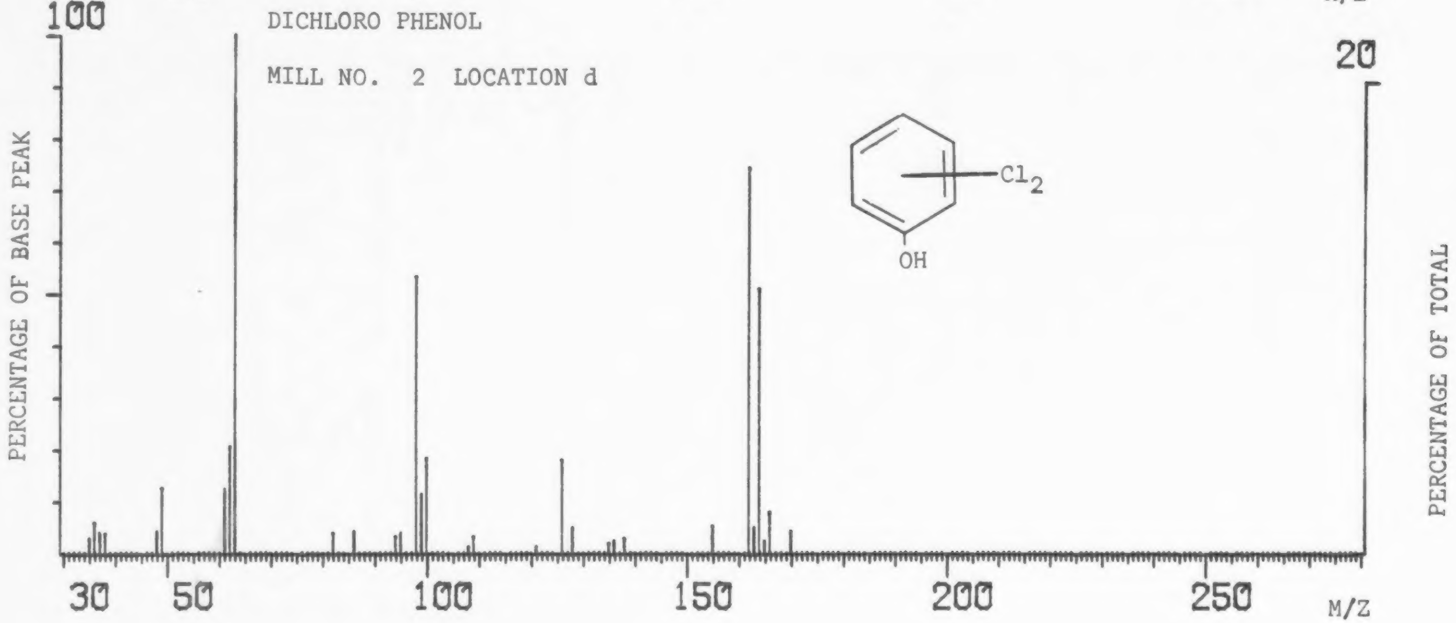

100 GUAIACOL
MILL NO. 11 LOCATION d
30
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


100
STANDARD 5-CHLORO INDOLE
20
Cl
N
H
30
50
100
150
200
250
M/Z
100
CHLORO INDOLE
MILL NO. 20
LOCATION d
10
Cl
N
H
30
50
100
150
200
250
M/Z
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL


100
STANDARD METHYL PALMITATE
> 250 X 5
10
$CH_3-(CH_2)_{14}-C(=O)OCH_3$
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

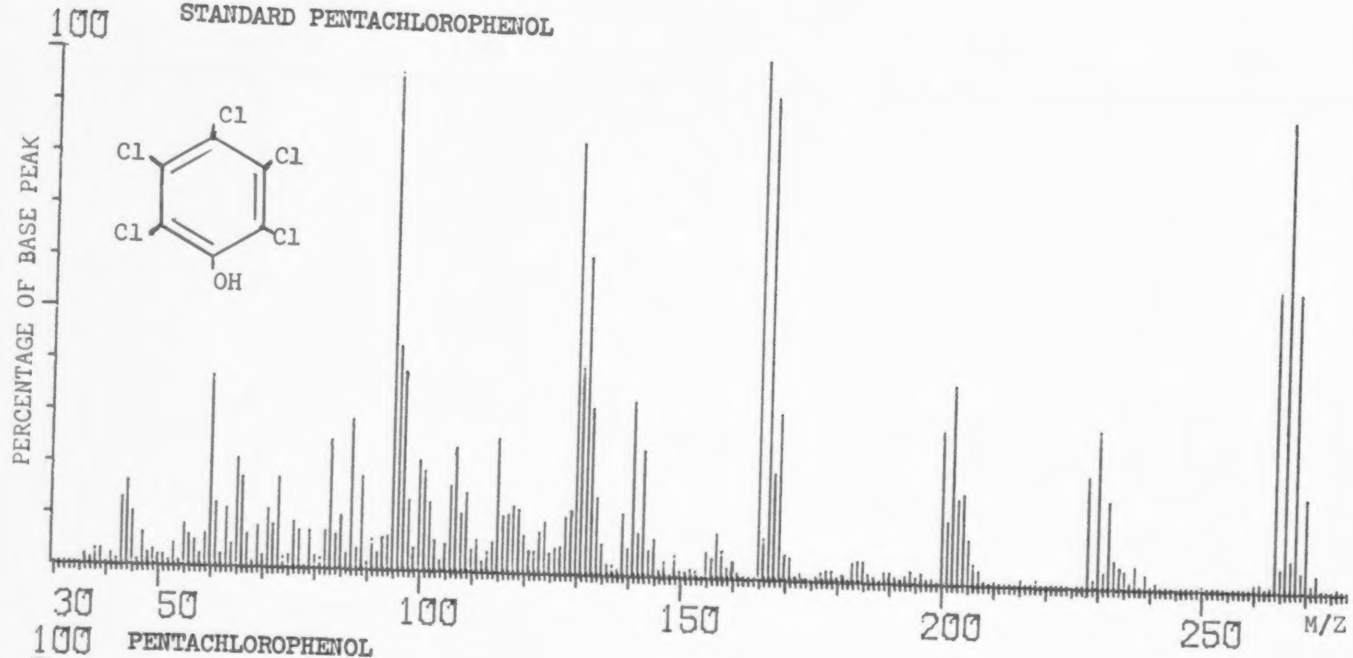

100
METHYL PALMITATE
MILL NO. 2
LOCATION d
> 150 X 3
25
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


STANDARD 2,4-DICHLORO PHENOL


DICHLORO PHENOL

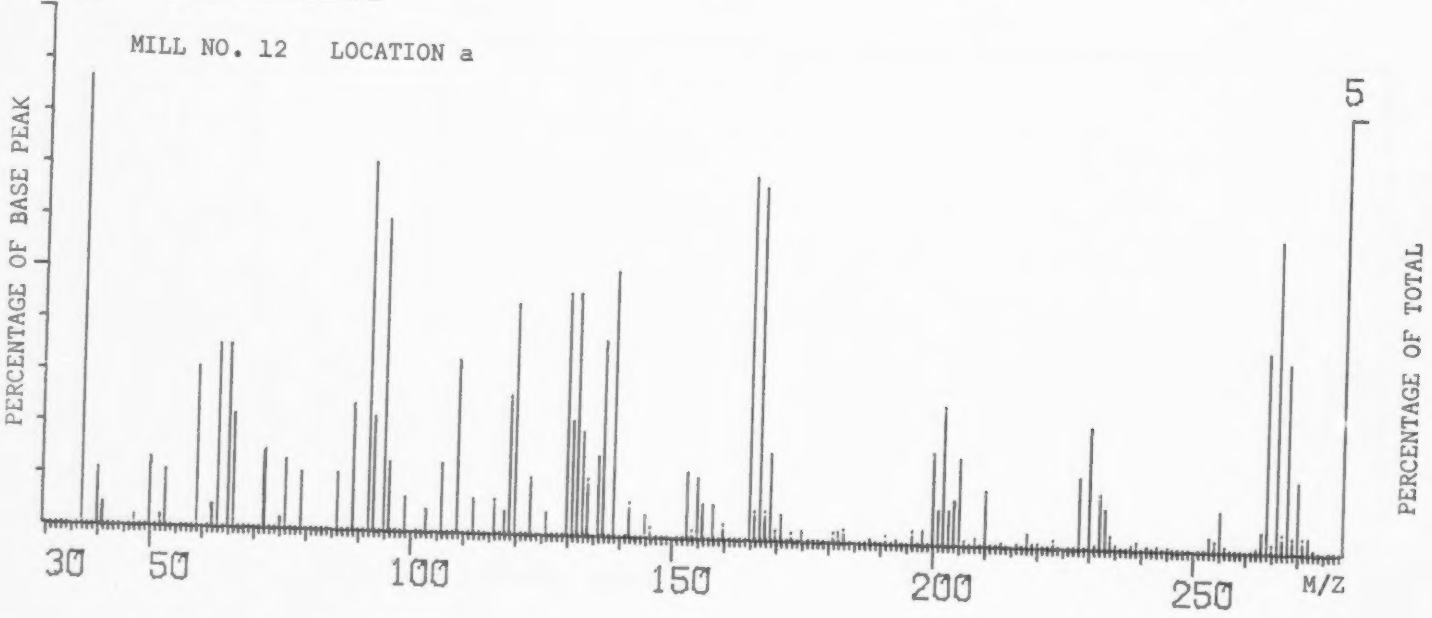
MILL NO. 2 LOCATION d

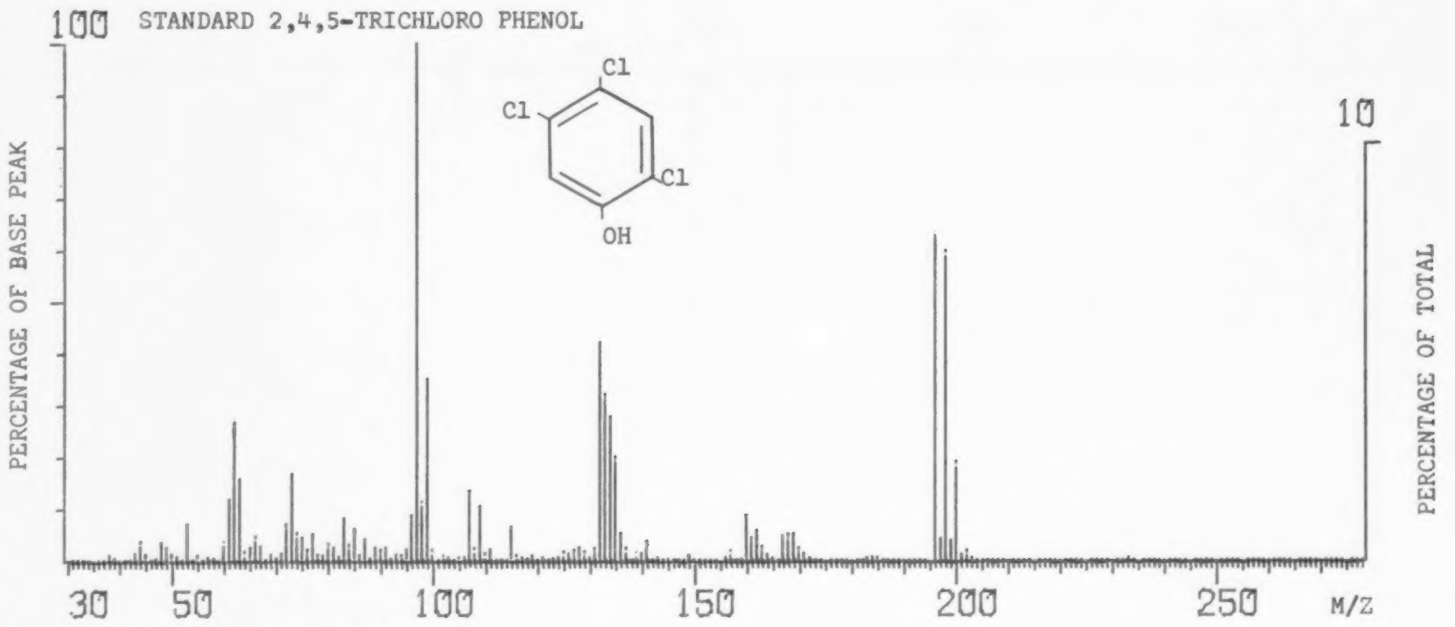
STANDARD PENTACHLOROPHENOL

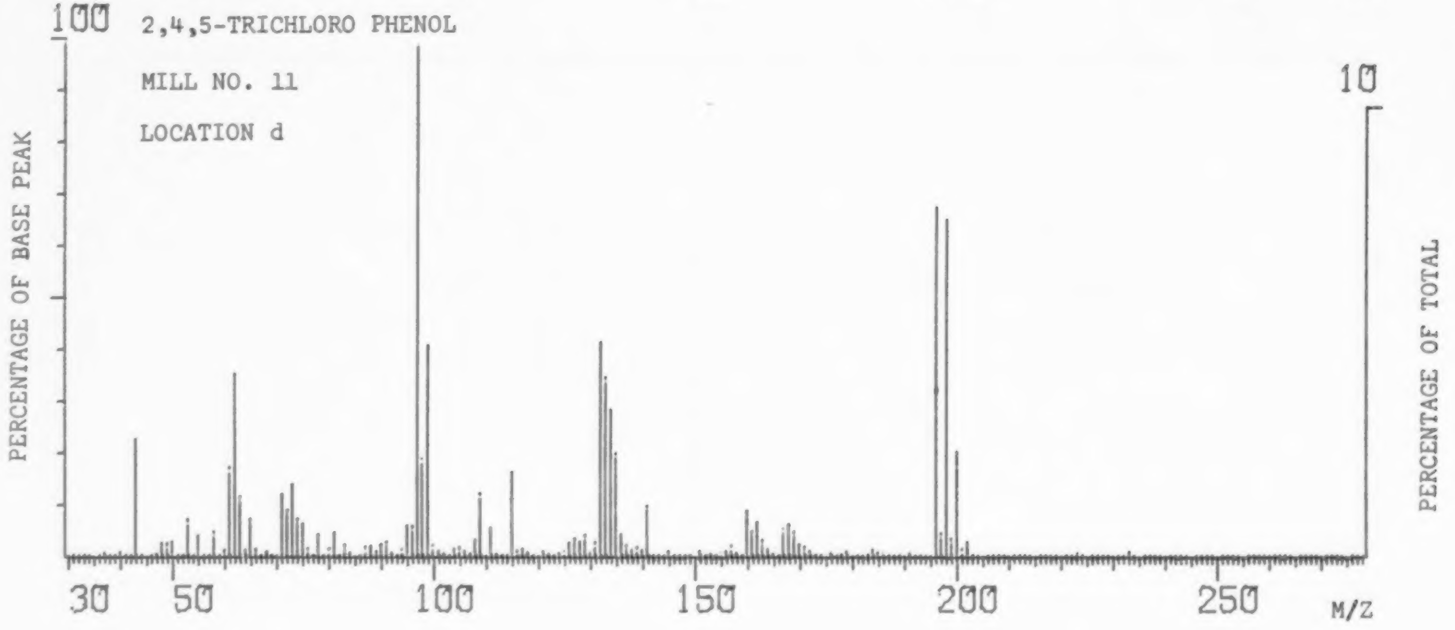


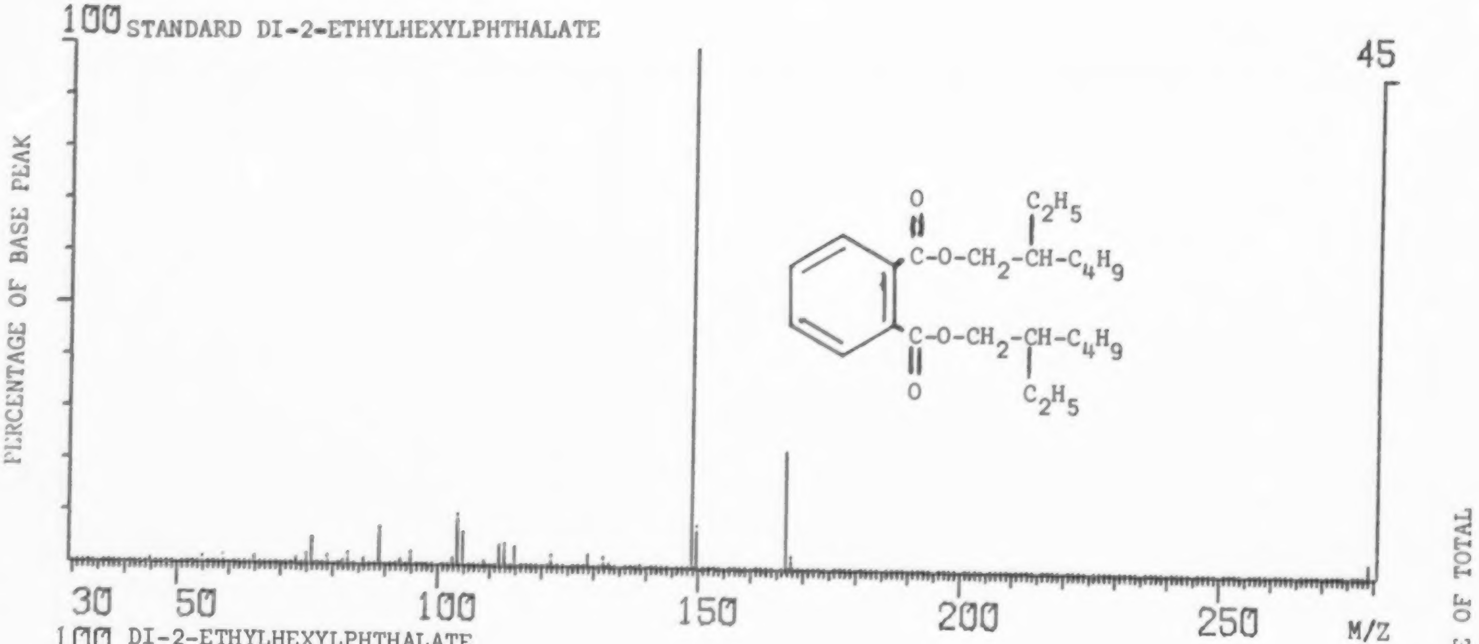
PENTACHLOROPHENOL

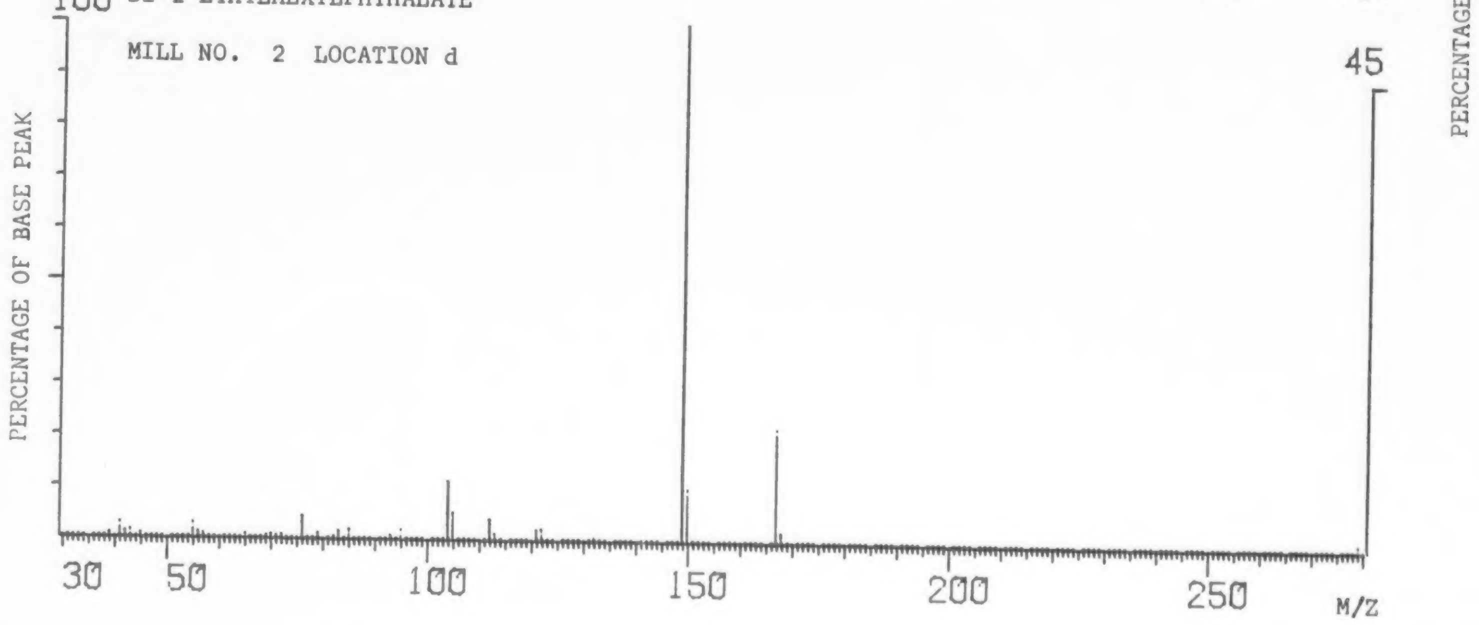
MILL NO. 12 LOCATION a

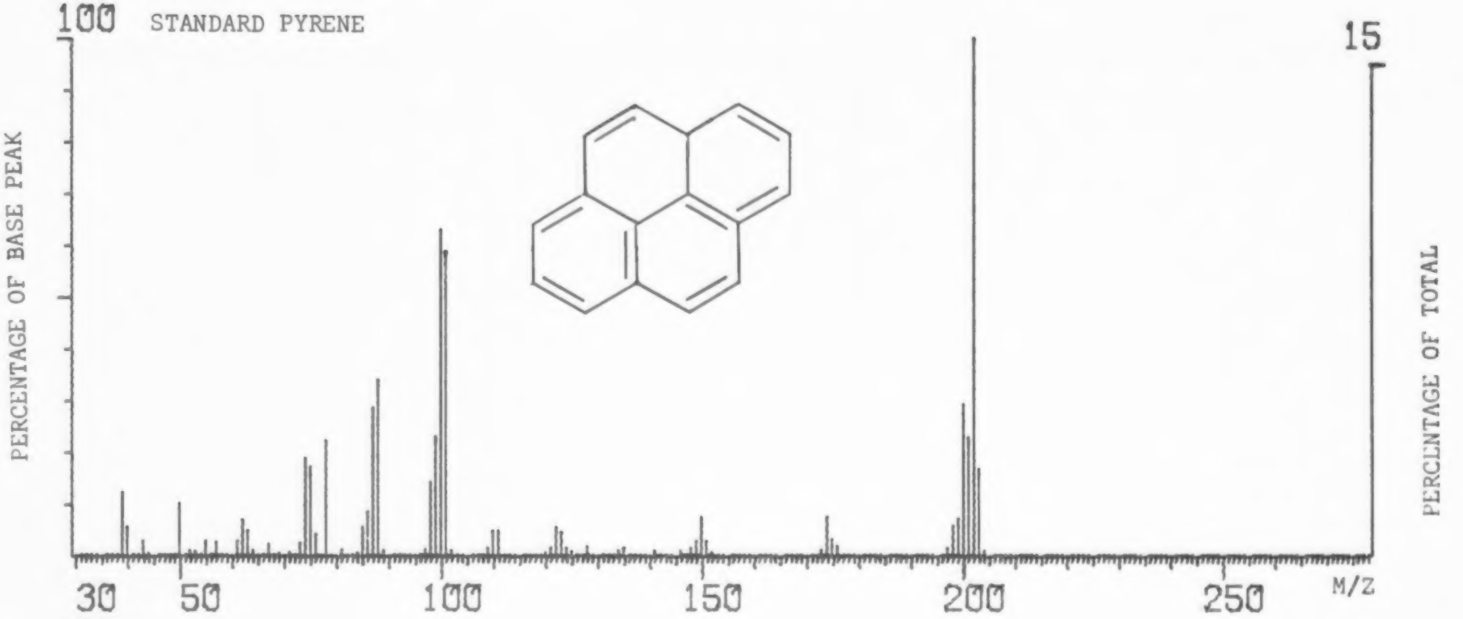


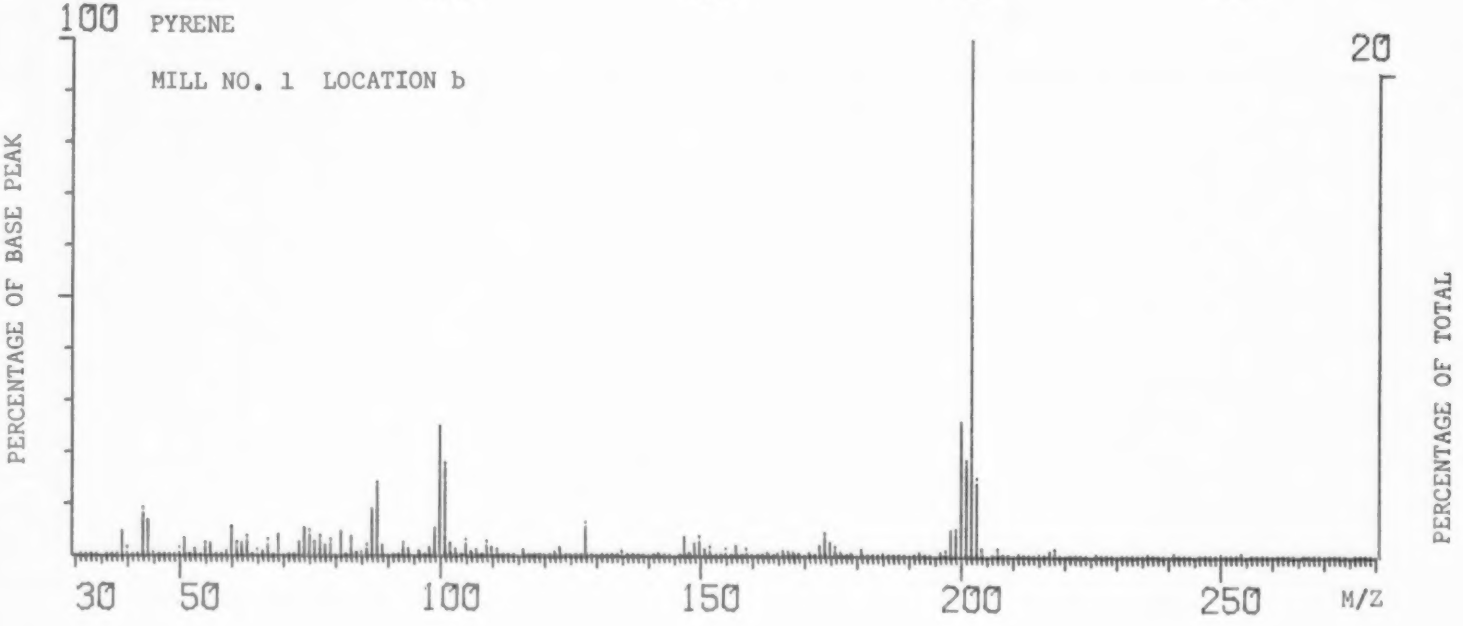

100
STANDARD 2,4,5-TRICHLORO PHENOL
Cl
Cl
Cl
OH
10
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

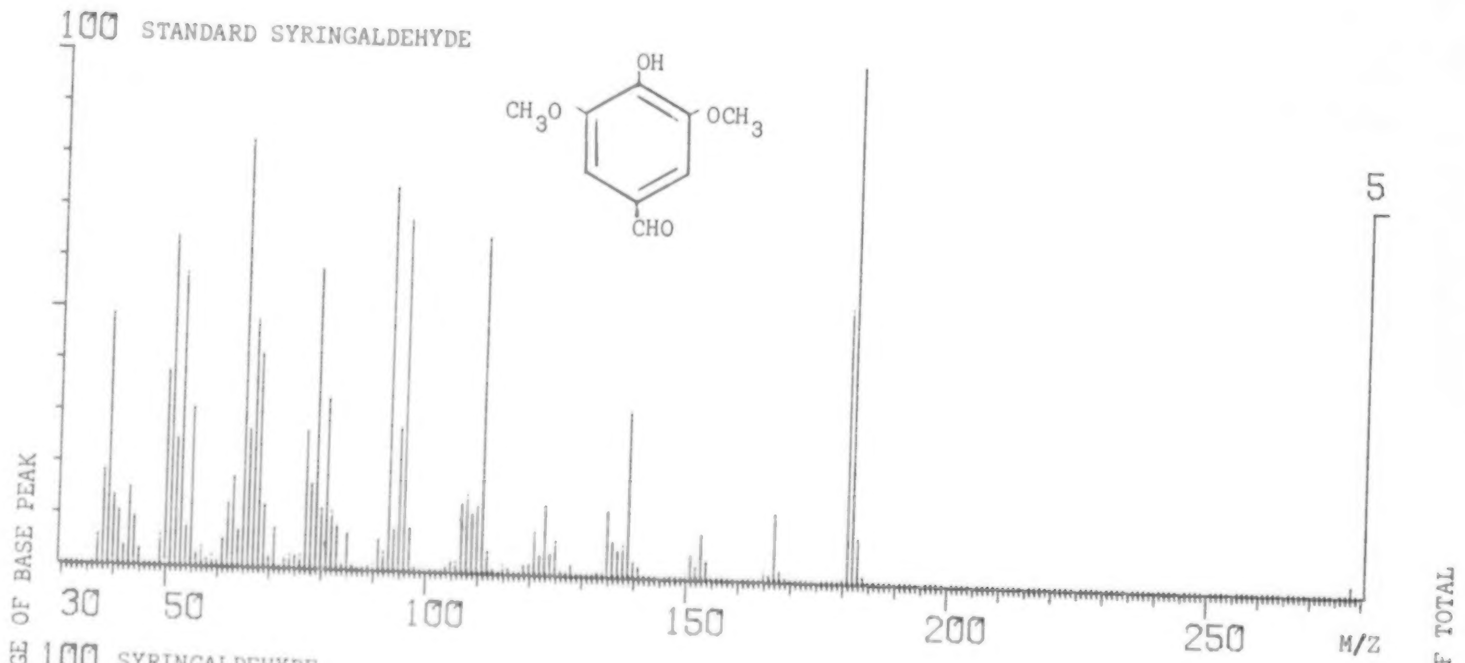

100
2,4,5-TRICHLORO PHENOL
MILL NO. 11
LOCATION d
10
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

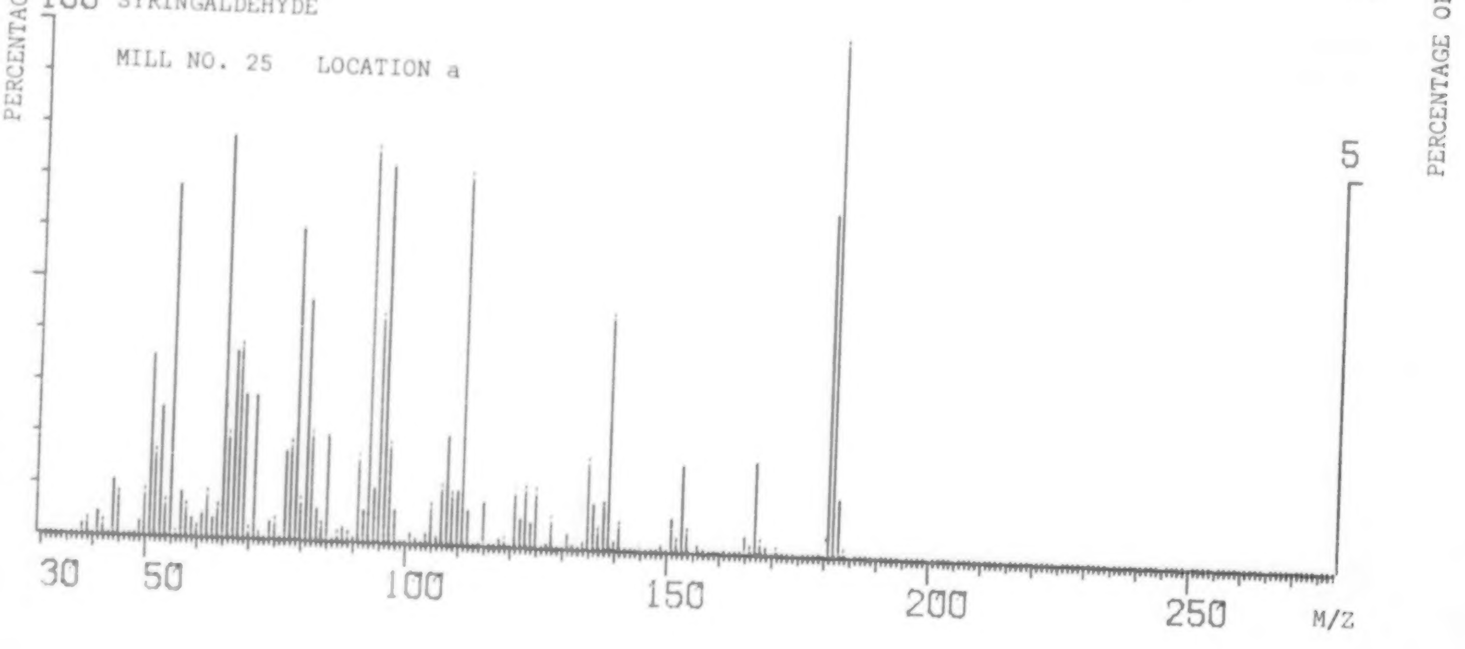

100
STANDARD DI-2-ETHYLHEXYLPHTHALATE
45
PERCENTAGE OF BASE PEAK
O
C-O-CH2-CH-C4H9
C2H5
C-O-CH2-CH-C4H9
O
C2H5
30
50
100
150
200
250
M/Z
PERCENTAGE OF TOTAL

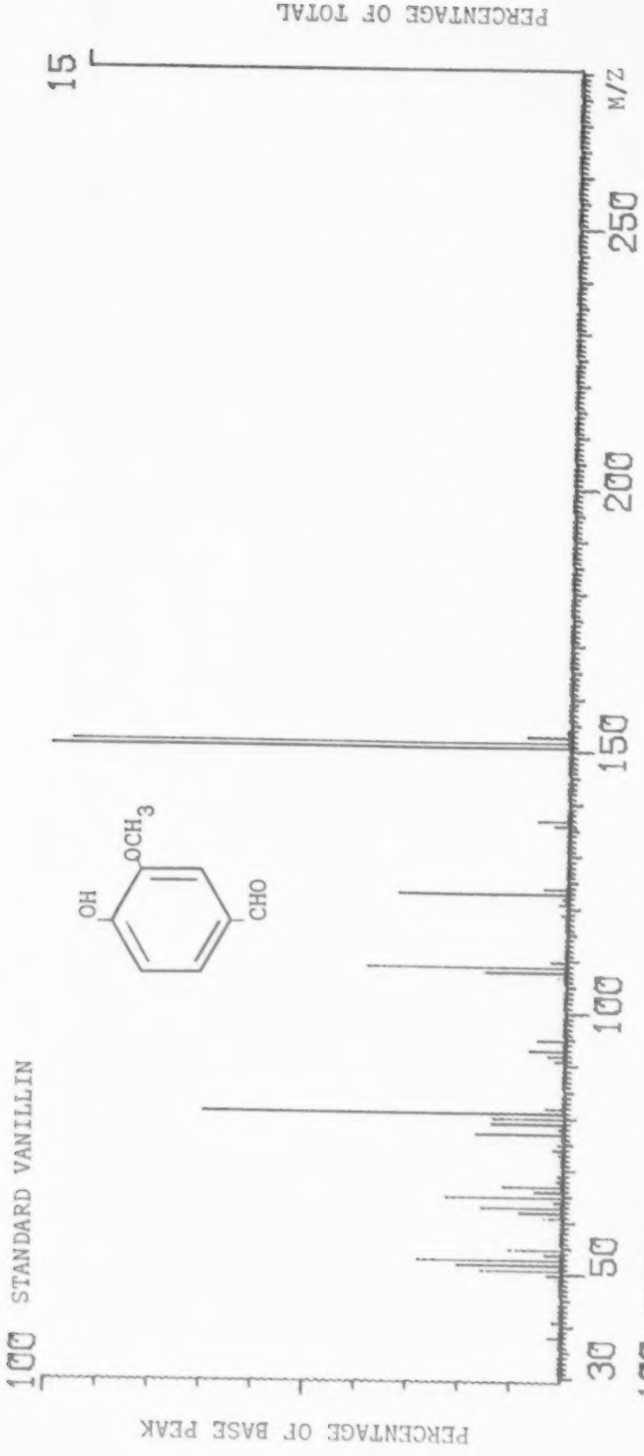

100
DI-2-ETHYLHEXYLPHTHALATE
MILL NO. 2 LOCATION d
45
PERCENTAGE OF BASE PEAK
30
50
100
150
200
250
M/Z

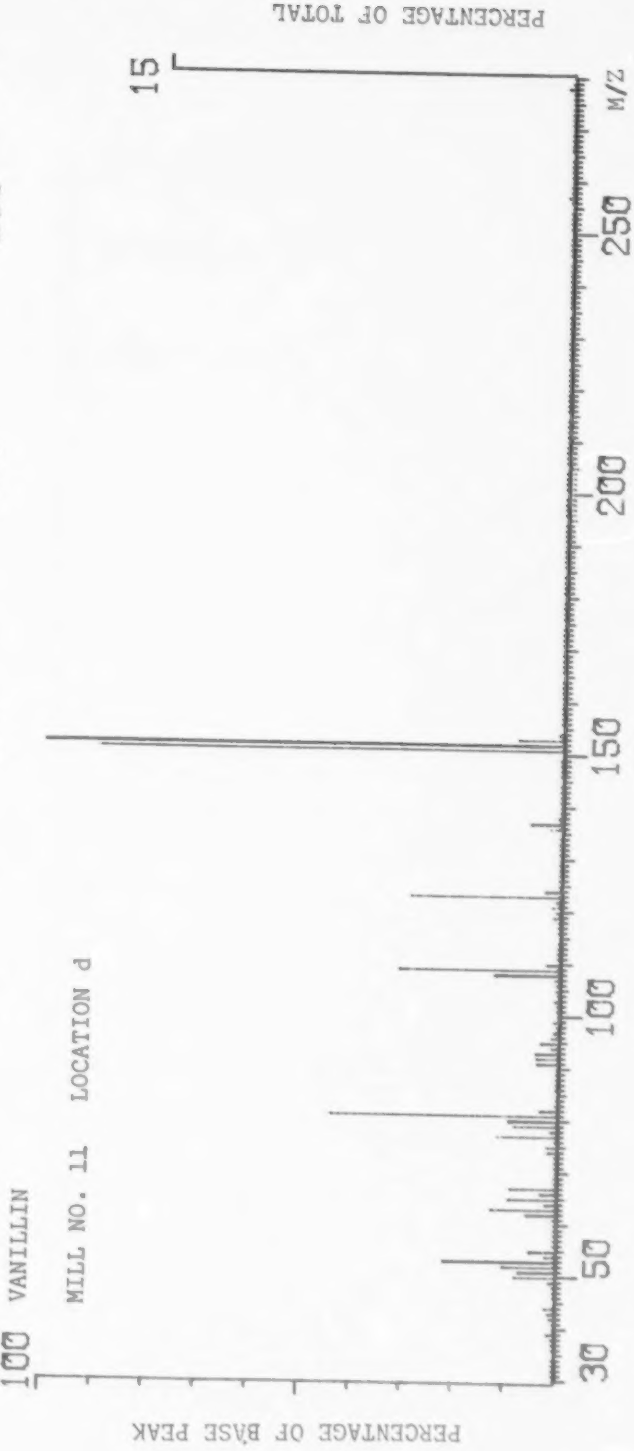

100
STANDARD PYRENE
15
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z

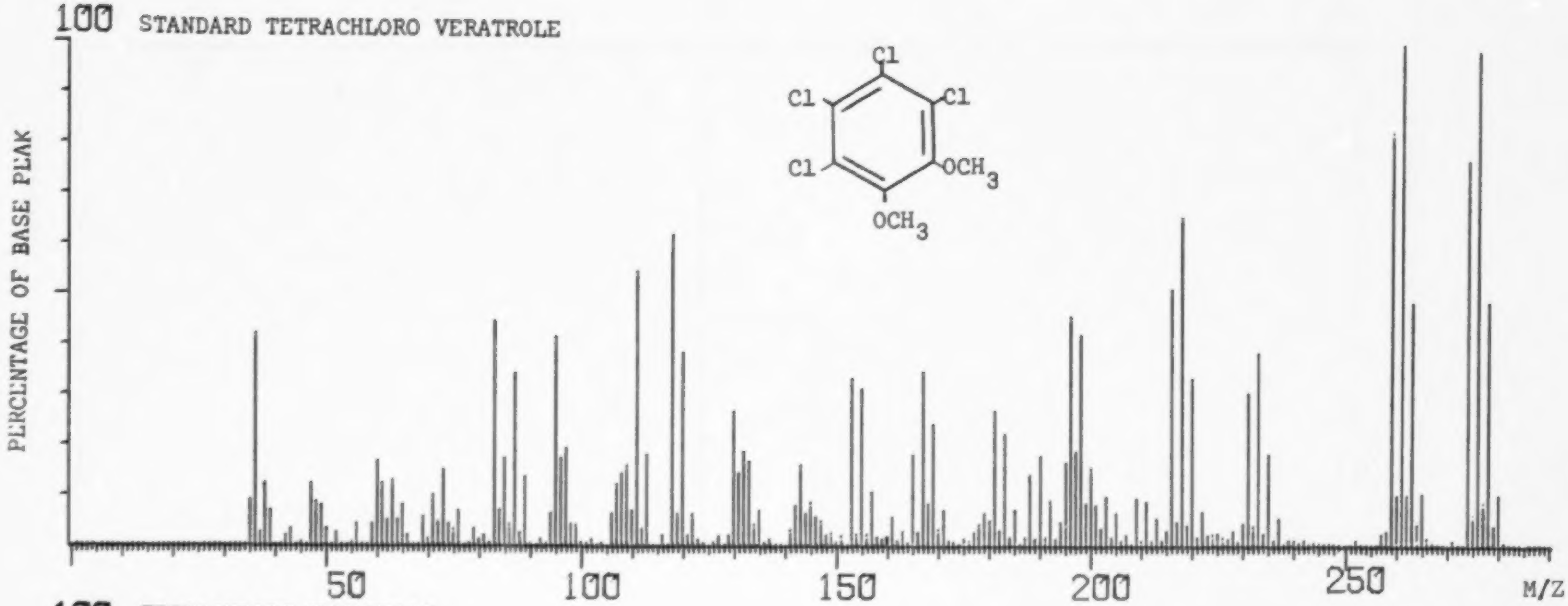

100
PYRENE
MILL NO. 1 LOCATION b
20
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


100
STANDARD SYRINGALDEHYDE
OH
CH3O
OCH3
CHO
5
30
50
100
150
200
250
M/Z
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL

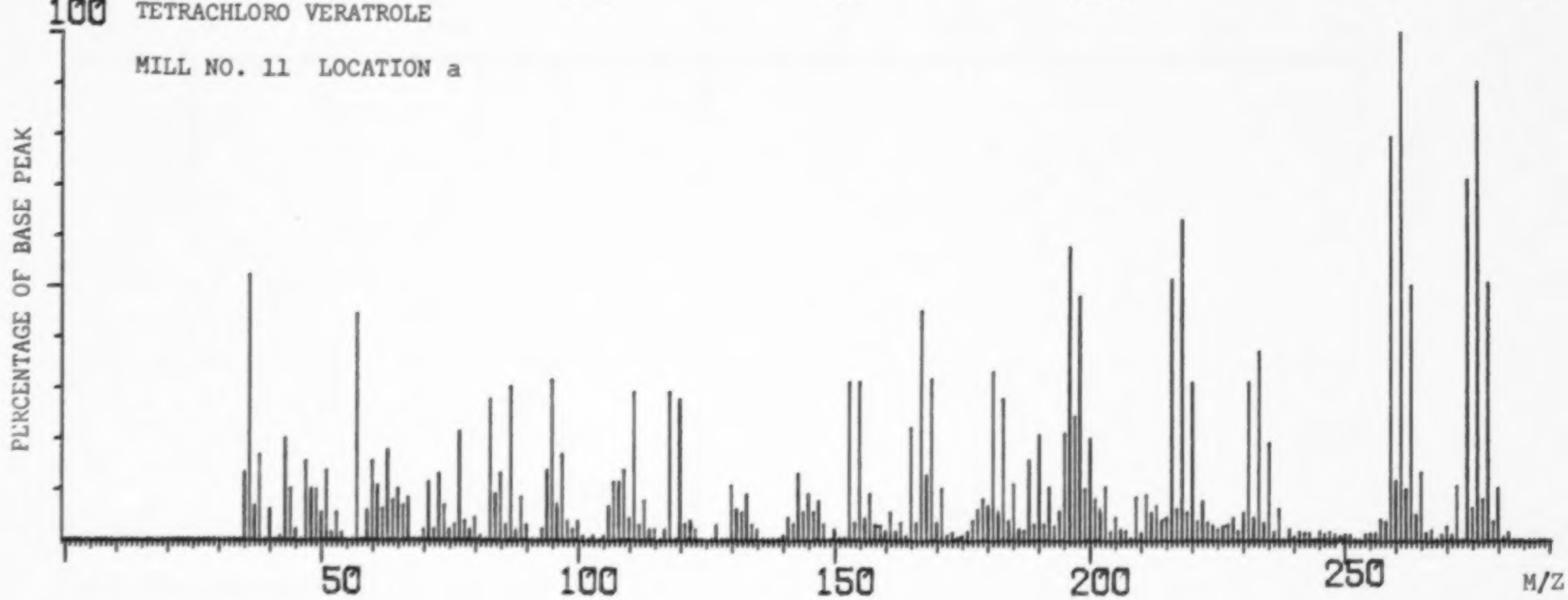

100
SYRINGALDEHYDE
MILL NO. 25 LOCATION a
5
30
50
100
150
200
250
M/Z


STANDARD VANILLIN
OH
OCH3
CHO
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
100
15
30
50
100
150
200
250
M/Z


VANILLIN
MILL NO. 11 LOCATION d
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
100
15
30
50
100
150
200
250
M/Z

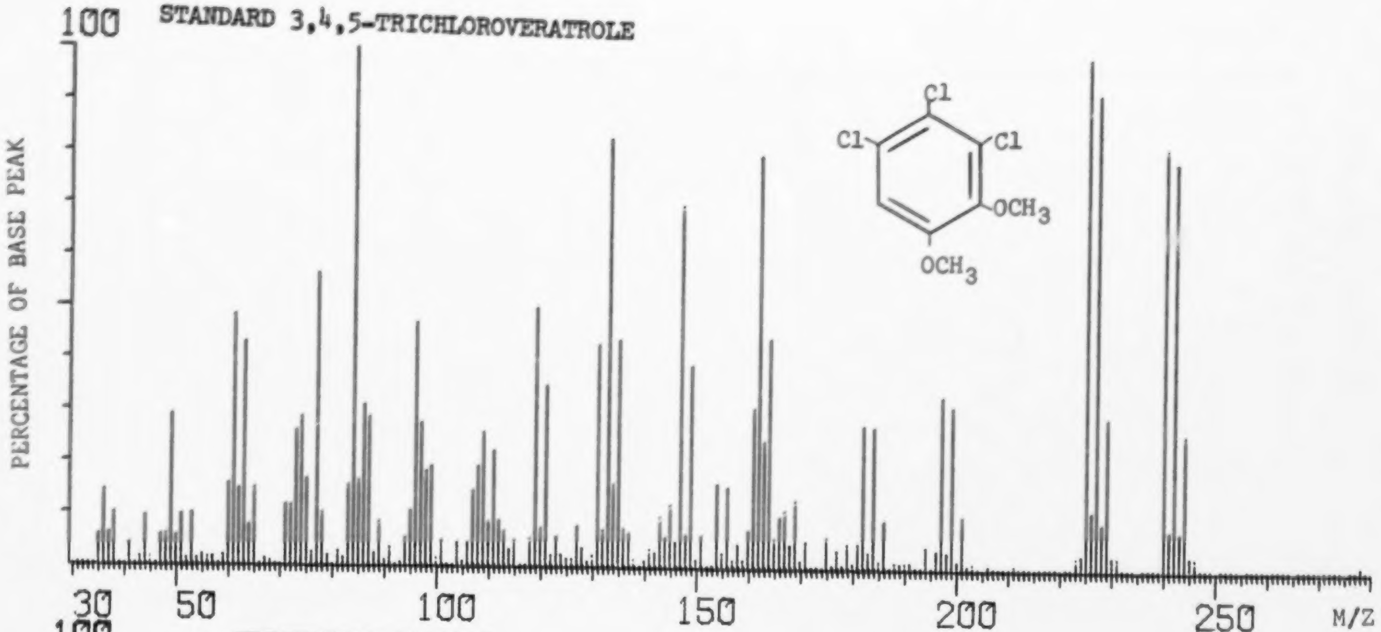


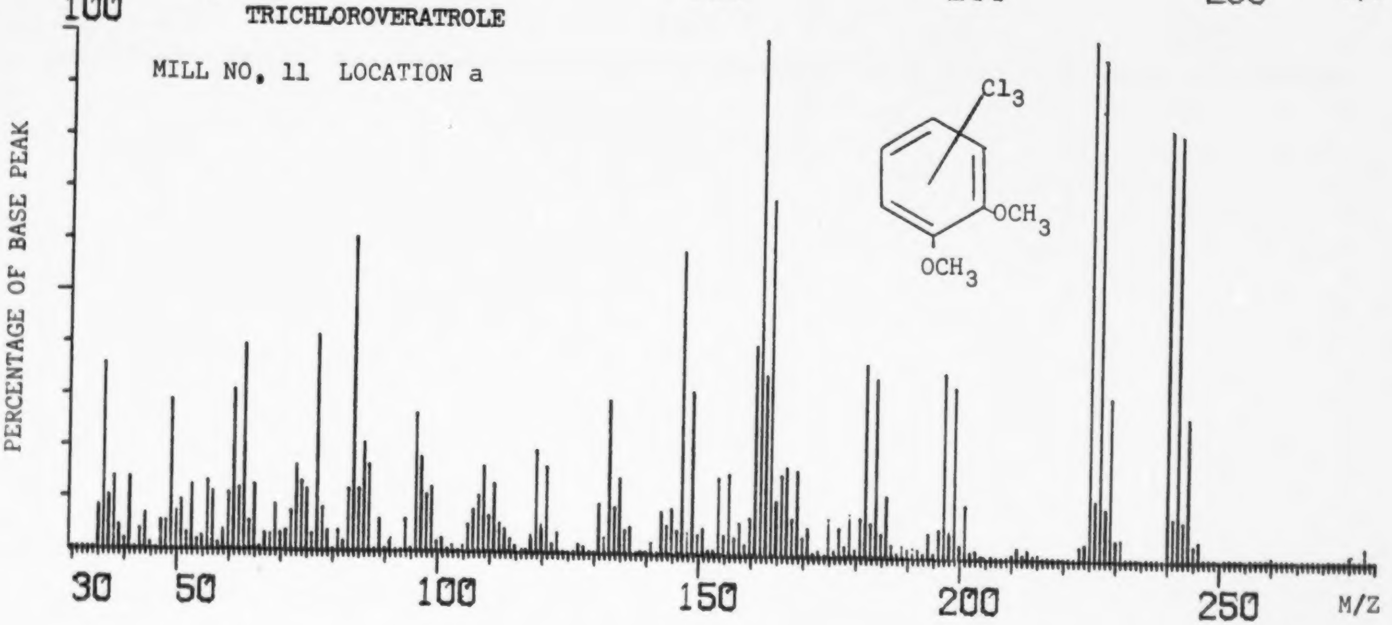
STANDARD TETRACHLORO VERATROLE



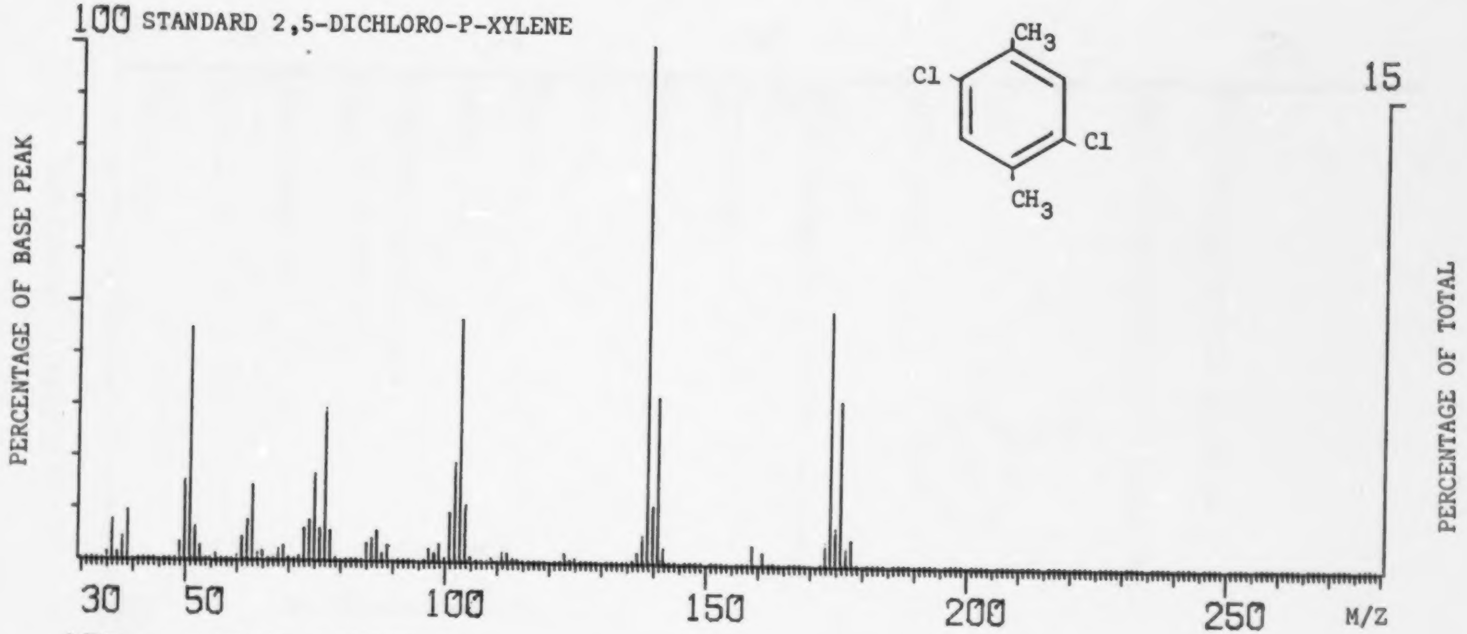
TETRACHLORO VERATROLE

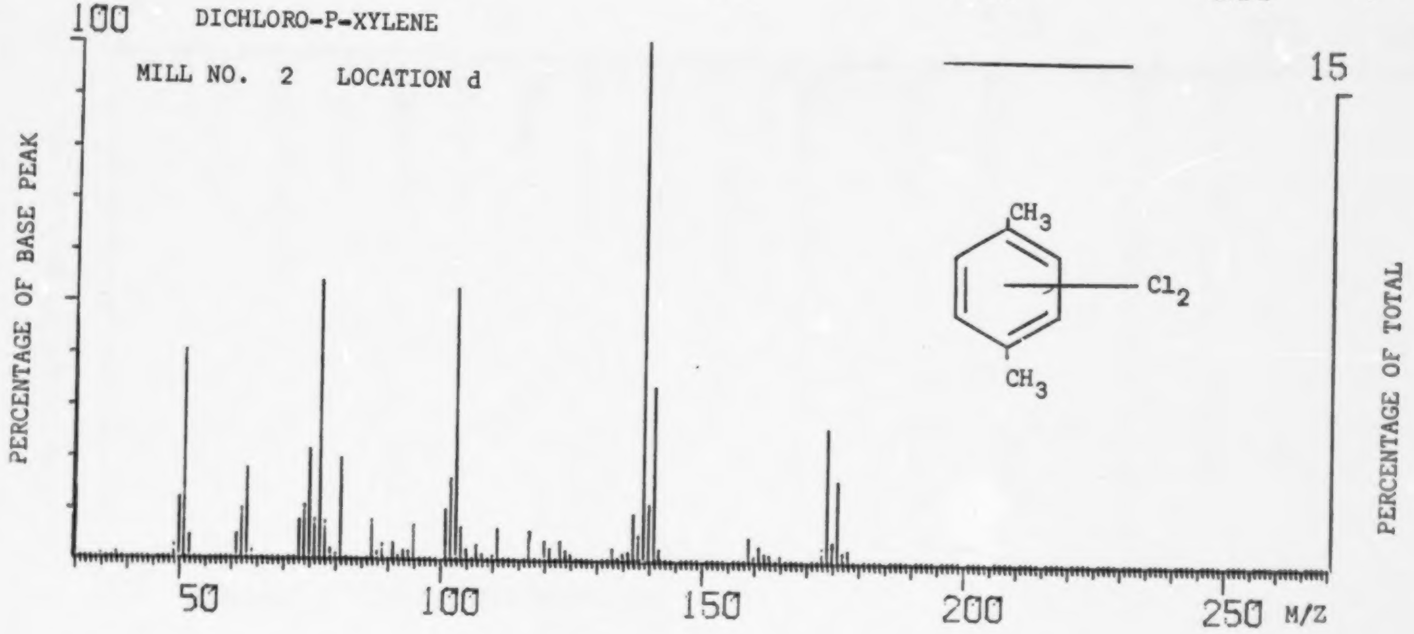
MILL NO. 11 LOCATION a


STANDARD 3,4,5-TRICHLOROVERATROLE


TRICHLOROVERATROLE

MILL NO. 11 LOCATION a


STANDARD 2,5-DICHLORO-P-XYLENE

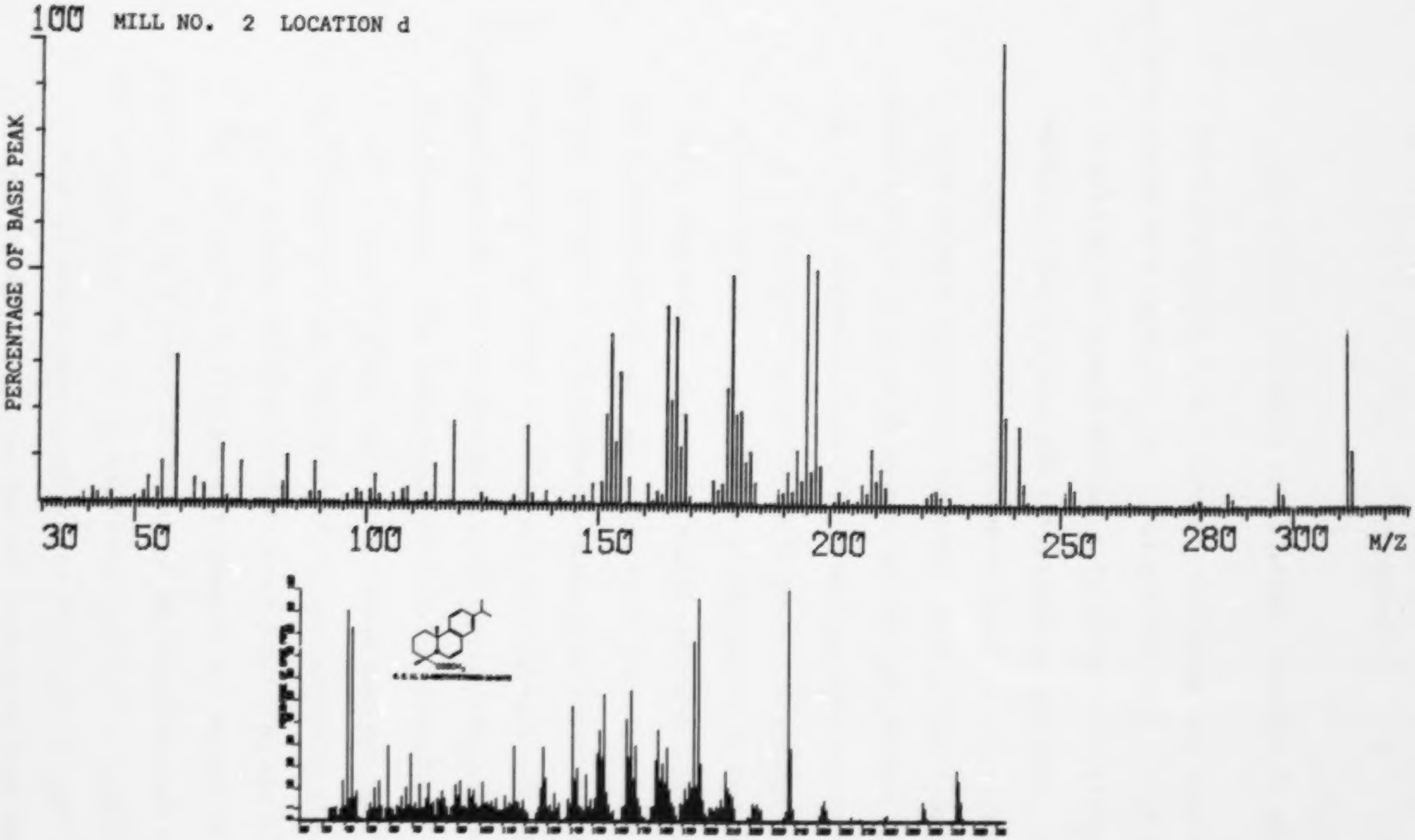

DICHLORO-P-XYLENE

MILL NO. 2 LOCATION d

APPENDIX E

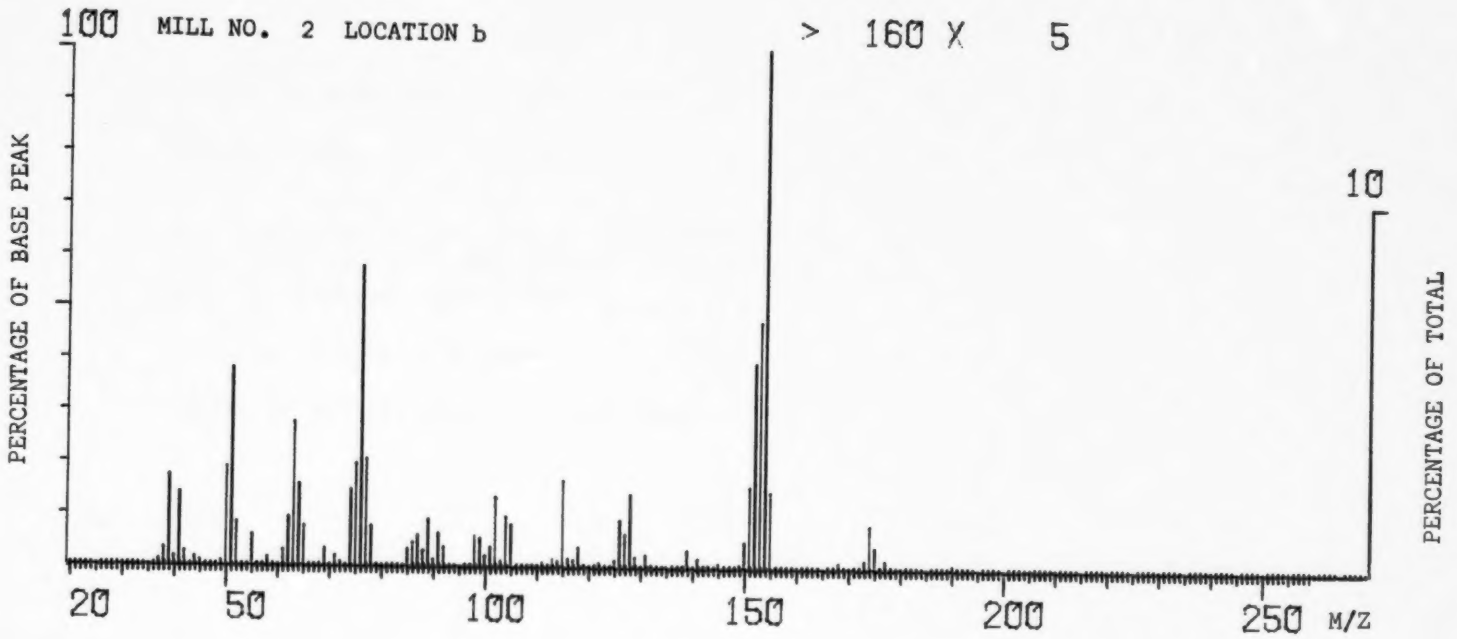
MASS SPECTRA OF COMPOUNDS IDENTIFIED BY LITERATURE COMPARISONS

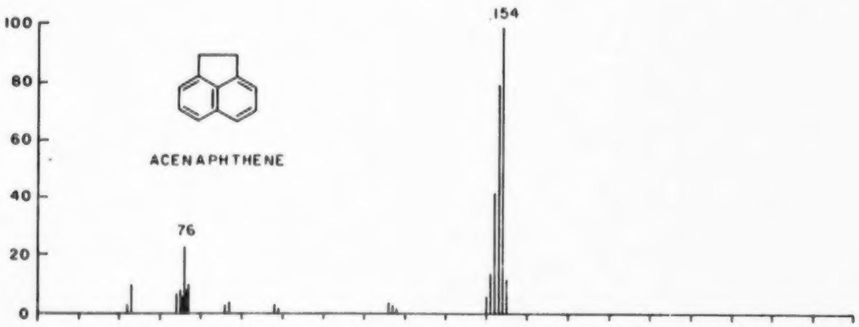
Appendix E includes some comparisons between sample spectra and those from the literature. Also included is a comparison spectra of chlorosyringaldehyde present in a sample with spectra of a reaction product synthesized in our laboratory. Chlorosyringaldehyde has not been previously reported in the environment. It was found in an acidic fraction of a sample from Mill 25, location A (influent to wastewater treatment), together with syringaldehyde, a common degradation product of hardwood lignin (Sarkanen, (39). To confirm the mass spectrum of chlorosyringaldehyde (E-17), the chlorination of syringaldehyde was attempted in our laboratory. A commercial standard of syringaldehyde was added to a solution of 5.25% sodium hypochlorite (commercial bleach) in aqueous acetic acid. The reaction proceeded overnight, after which time the reaction product was extracted with dichloromethane, evapo-concentrated to dryness redissolved in acetone, and then injected into the GC/MS. A total ion chromatogram indicated both unreacted syringaldehyde and newly formed chlorosyringaldehyde. Not only did the retention times of these compounds match those present in the sample, but the mass spectra also were closely matched. The apparent isotopic molecular ions of chlorosyringaldehyde (page E-17) at m/z 216 and 218 are consistent for a compound with one chlorine atom. The two ions as well as the fragment ions m/z 215, 201, 173, 145, 130, 127 and others have been shifted 34 mass units higher, which is consistent with the addition of a chlorine atom at one of the two remaining reactive sites on the ring. A very small of dichlorosyringaldehyde was also detected in the reaction product, but was not found in the sample.



Tentative Identification METHYL 6,8,11,13-ABIETATETRAEN-18-OATE

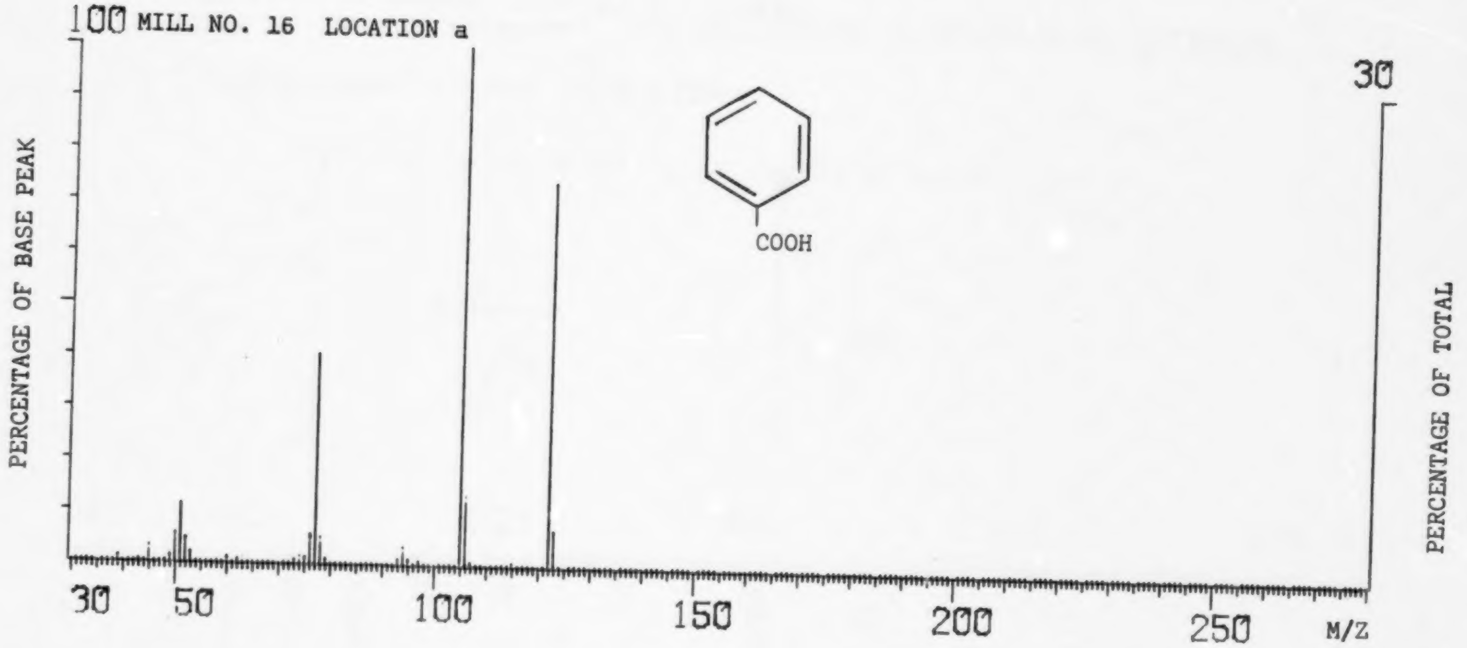
Keith, L.H. (Ed.). Analysis of Organic Compounds in Two Kraft Mill Wastewaters, EPA Report No. 660/4-75-005, 99 p. June (1975).





Tentative Identification ACENAPHTHENE

Safe, S. and O. Hutzinger. Mass Spectrometry of Pesticides and Pollutants. CRC Press, Cleveland, Ohio, 220 p. (1973).

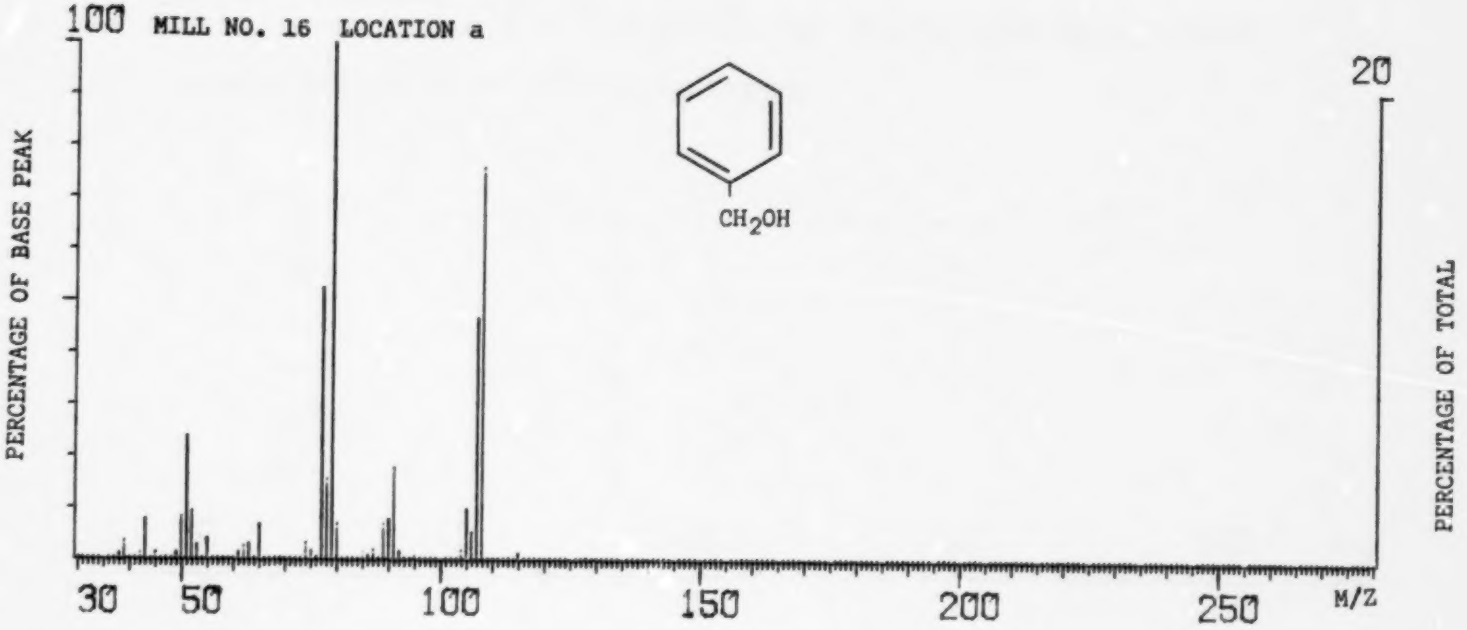


Tentative Identification BENZOIC ACID

Based on Tabular Data From:

Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 1, Page 691.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	105	122	77	51	50	106	78	123
PERCENT OF BASE PEAK	100	82	69	27	14	8	7	6

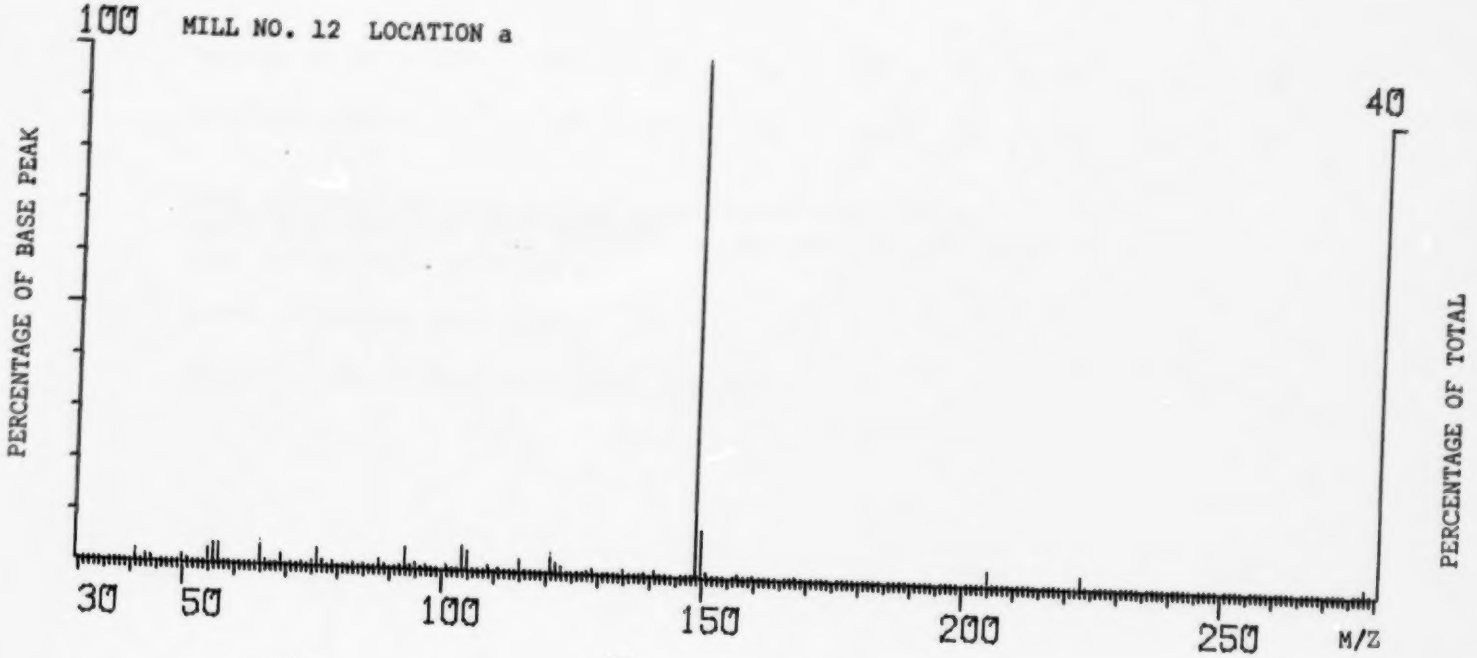


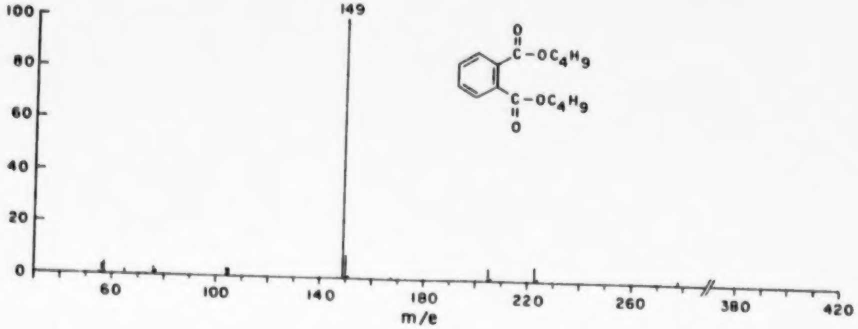
Tentative Identification BENZYL ALCOHOL

Based on Tabular Data From:

Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 3, Page 2105.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

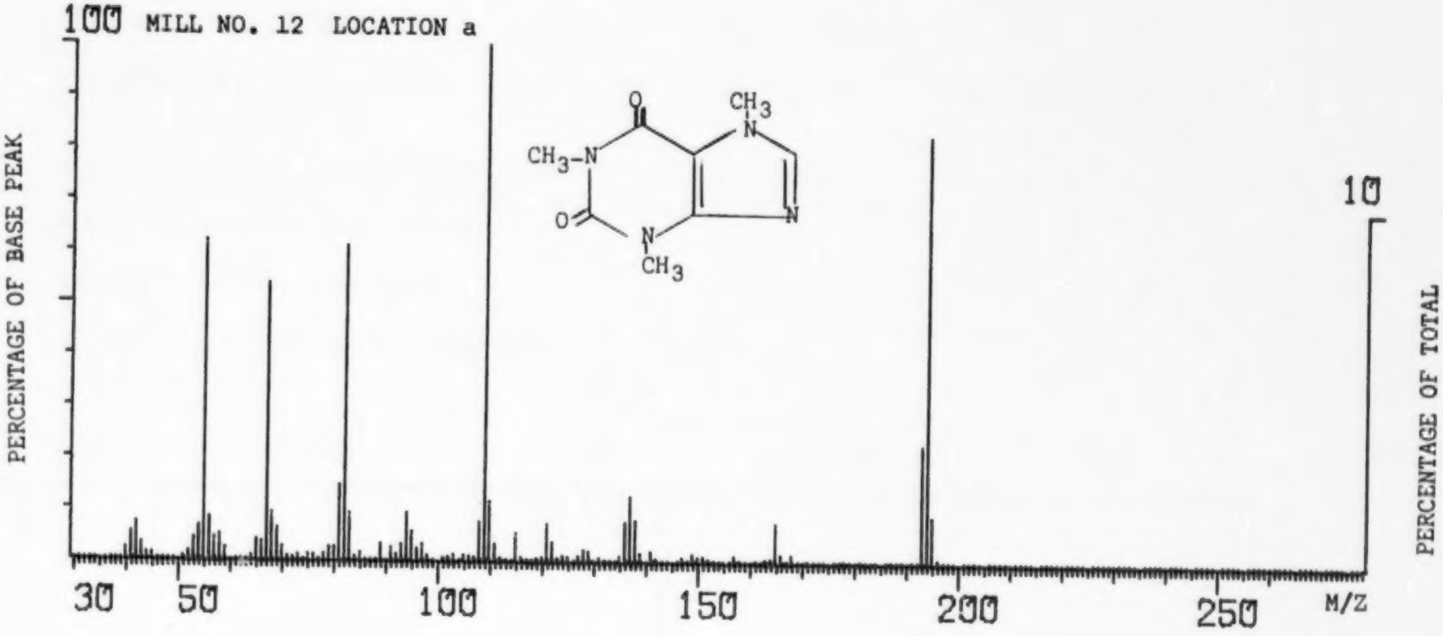
FRAGMENT IONS	79	108	107	77	51	91	78	50
PERCENT OF BASE PEAK	100	87	69	55	22	19	11	10





Tentative Identification DI-n-BUTYLPHTHALATE

Safe, S. and O. Hutzinger. Mass Spectrometry of Pesticides and Pollutants. CRC Press, Cleveland, Ohio, 220 p. (1973).

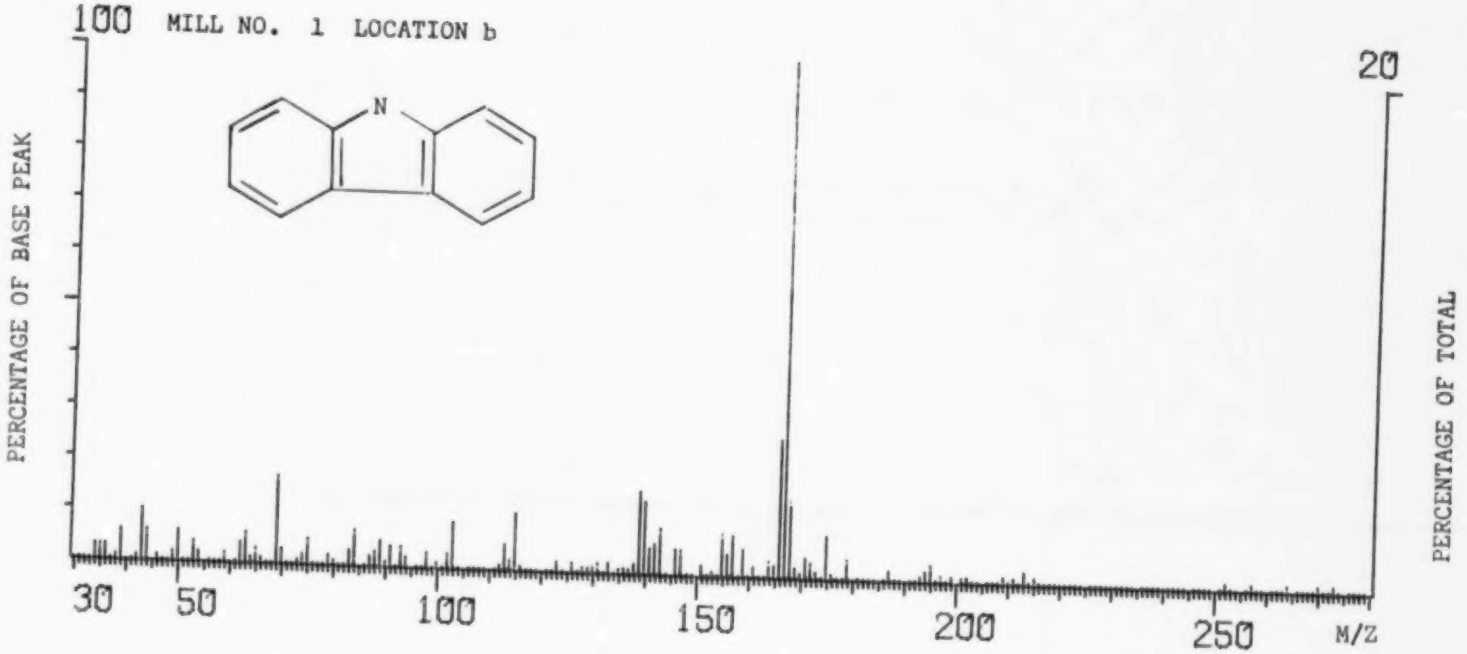


Tentative Identification CAFFEINE

Based on Tabular Data From:

Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 1, Page 868.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	194	109	55	67	82	15	18	42
PERCENT OF BASE PEAK	100	59	37	23	18	15	11	11

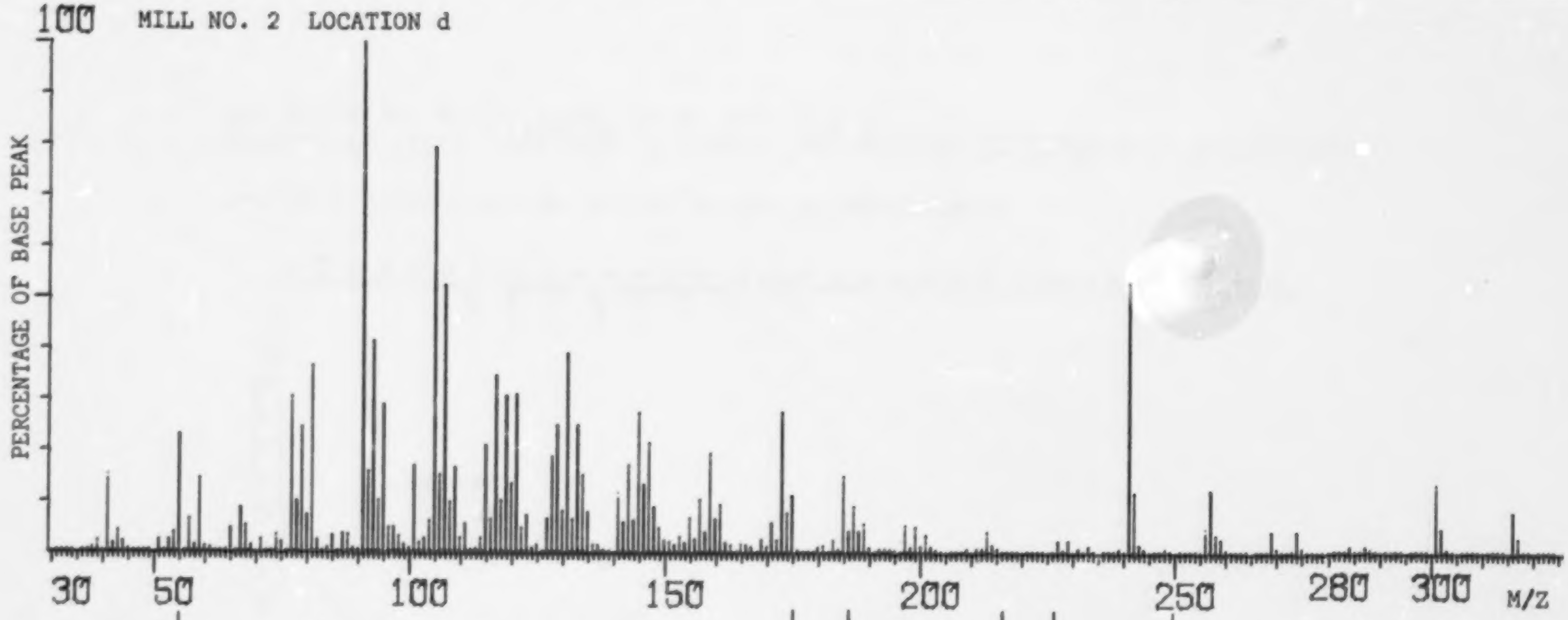


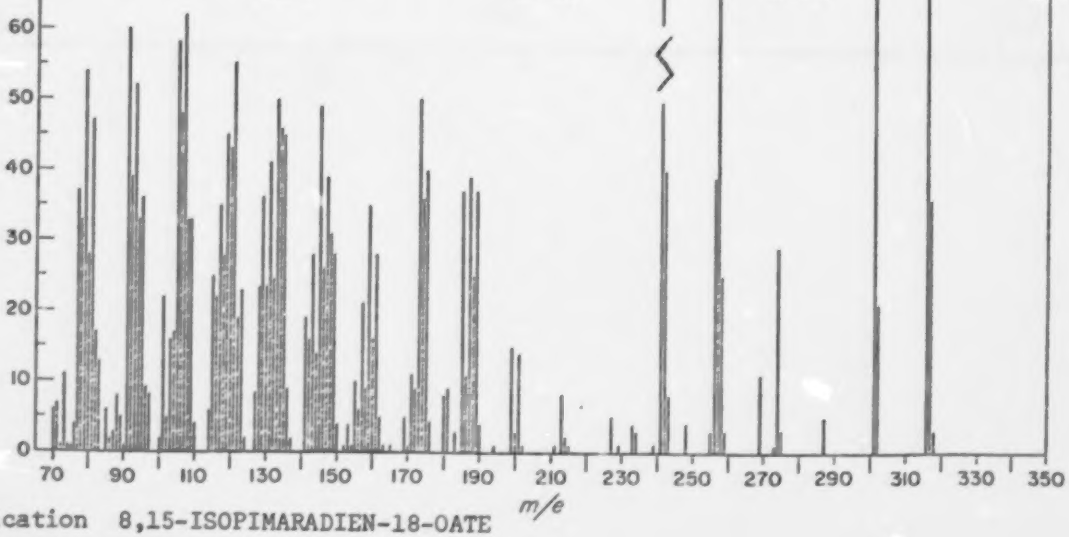
Tentative Identification CARBAZOLE

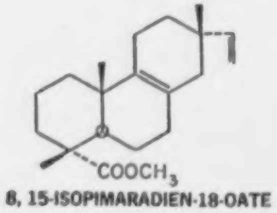
Based on Tabular Data From:

Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 3, Page 2457.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	167	166	139	168	140	83.5	70.5	63
PERCENT OF BASE PEAK	100	26	17	16	11	9	5	4



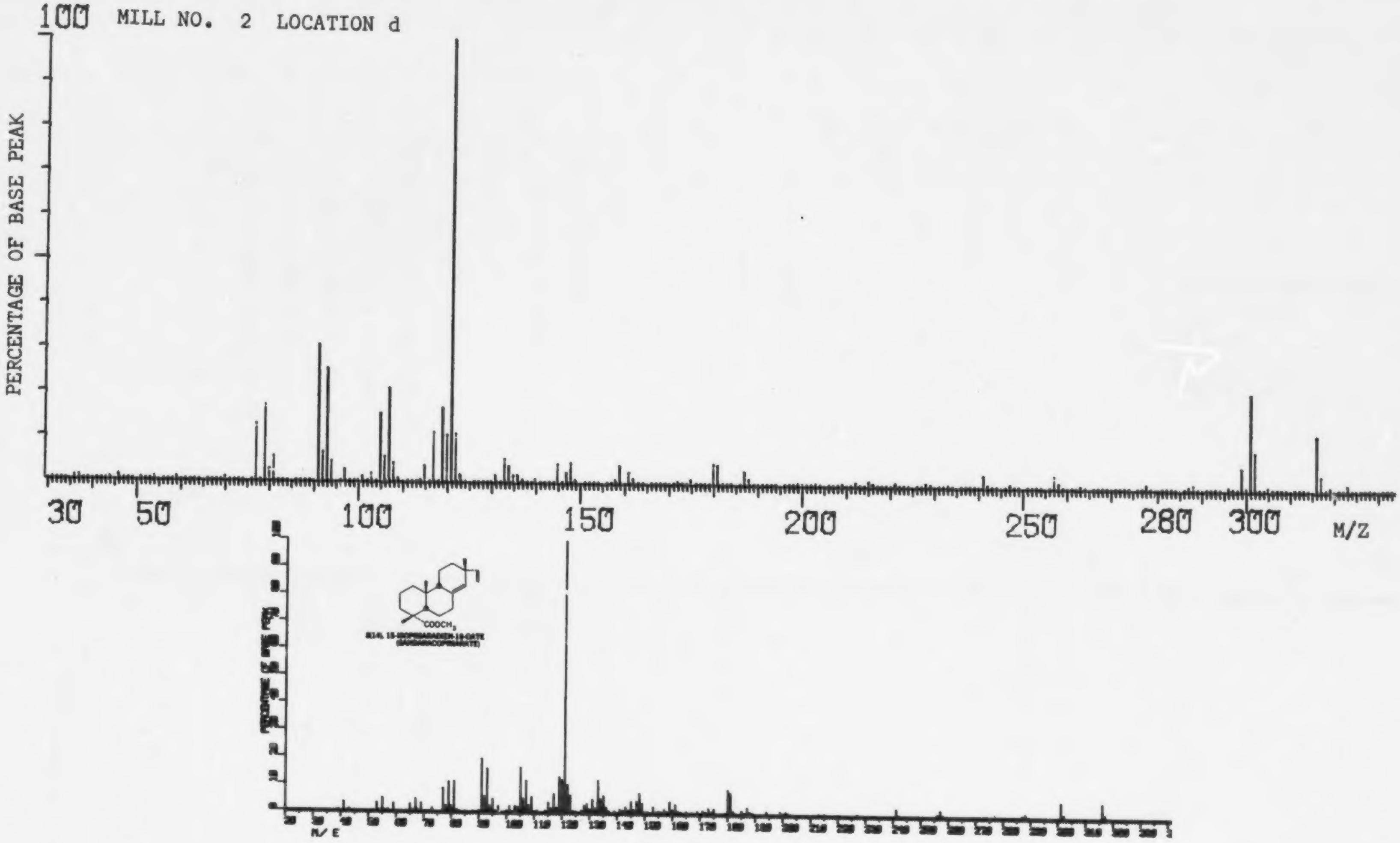




8, 15-ISOPIMARADIEN-18-OATE

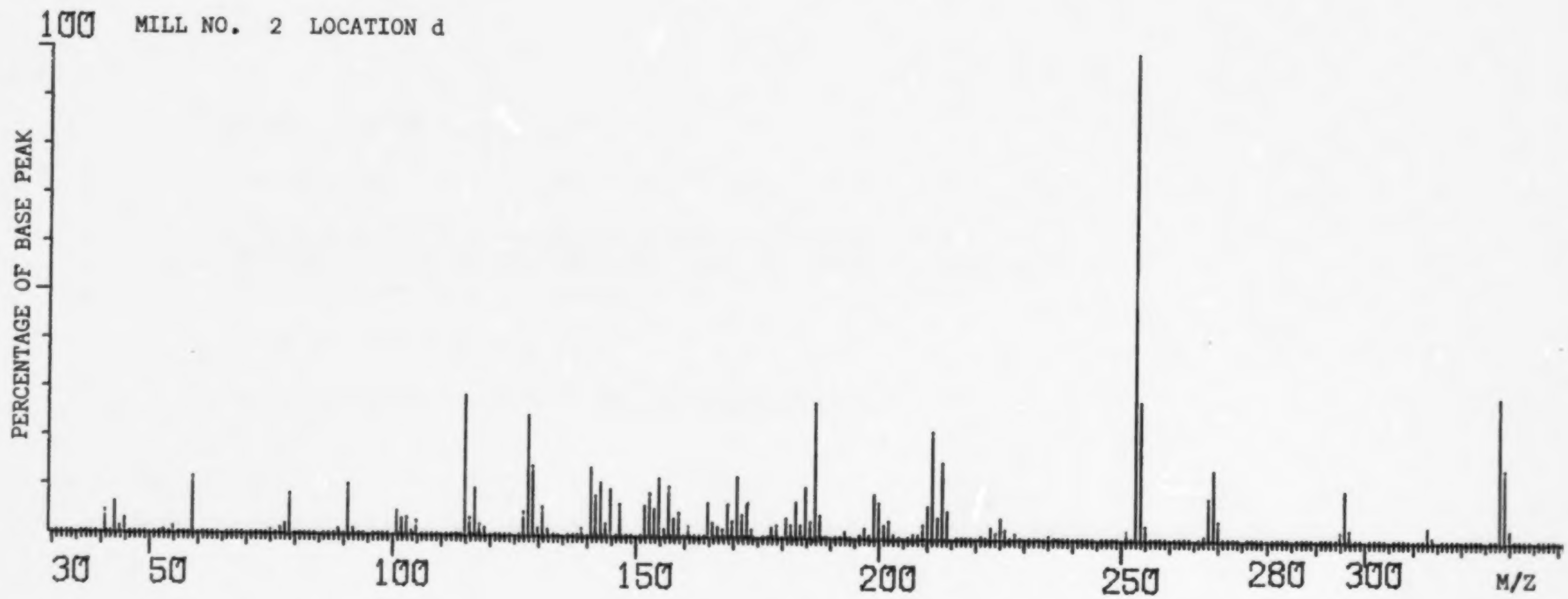
Tentative Identification 8,15-ISOPIMARADIEN-18-OATE

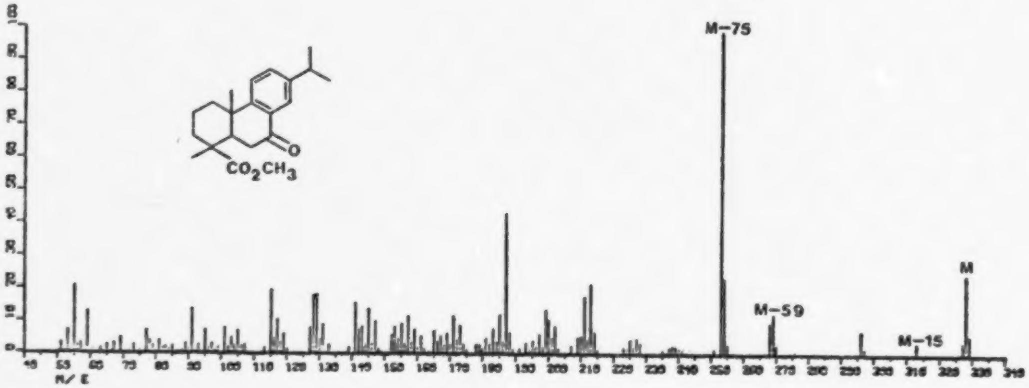
Zinkel, D.F., L. Zank and M.F. Wesolowski. Diterpene Resin Acids -- A Compilation of Infrared, Mass, Nuclear Magnetic Resonance, Ultraviolet Spectra and Gas Chromatographic Retention Data (of the Methyl Esters). USDA, Forest Products Laboratory, Madison, WI 174 p. (1971).



Tentative Identification 8,(14),15-ISOPIMARADIEN-18-OATE

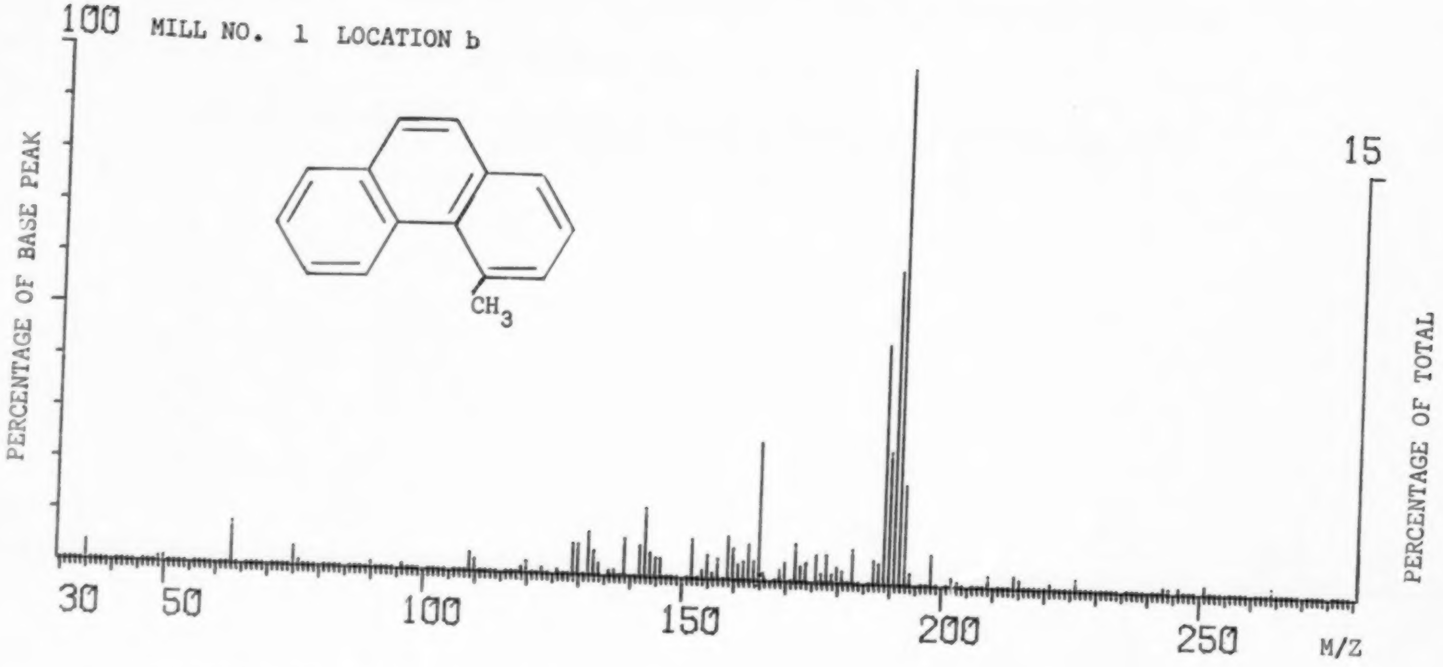
Keith, L.H. (Ed.). Analysis of Organic Compounds in Two Kraft Mill Wastewaters, EPA Report No. 660/4-75-005, 99 p. June (1975).





Tentative Identification METHYL OXODEHYDROABIETATE

Keith, L.H. (Ed.). Identitication and Analysis of Organic Pollutants in Water. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich, (1976). Page 835

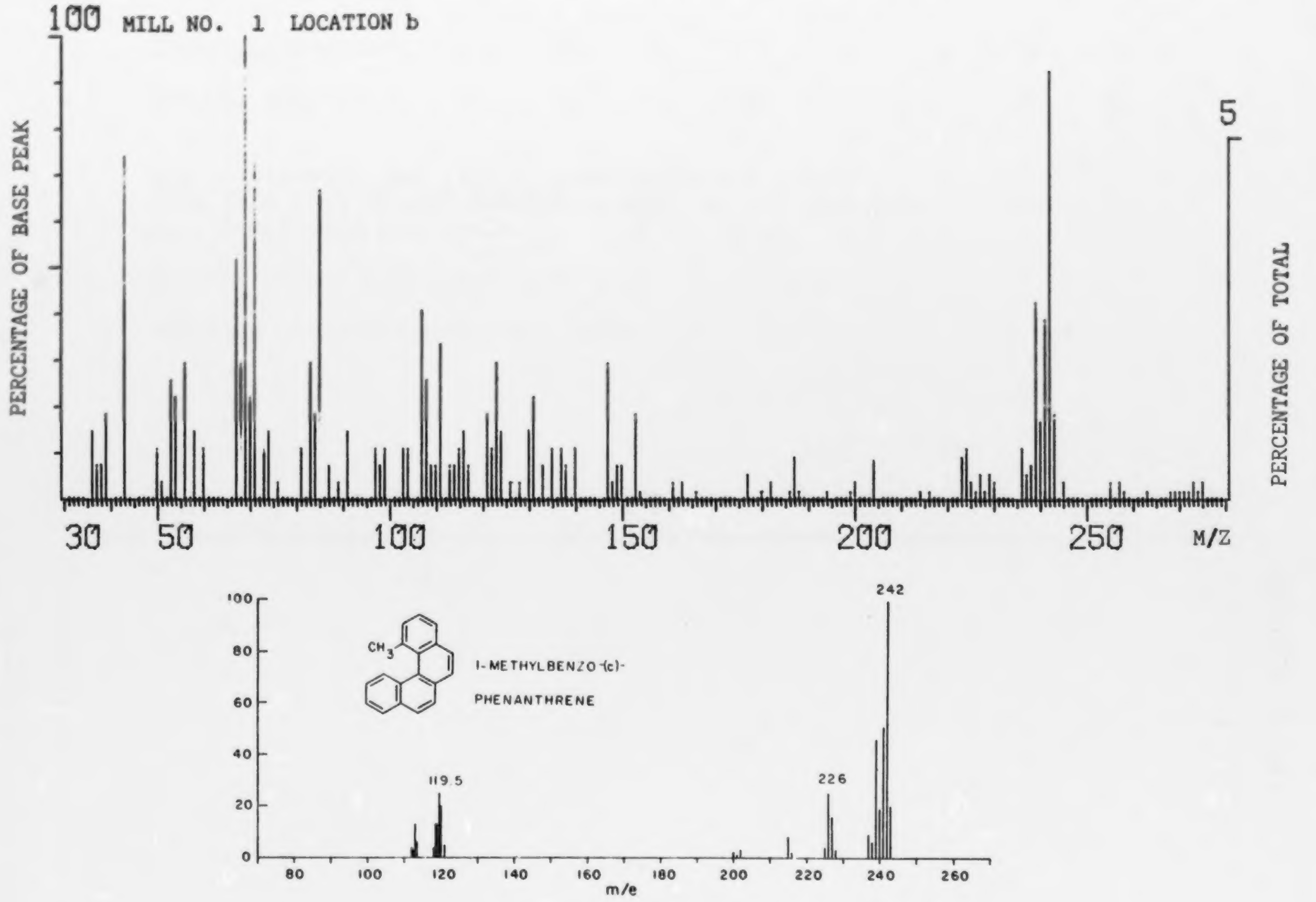


Tentative Identification 4-METHYL PHENANTHRENE

Based on Tabular Data From:

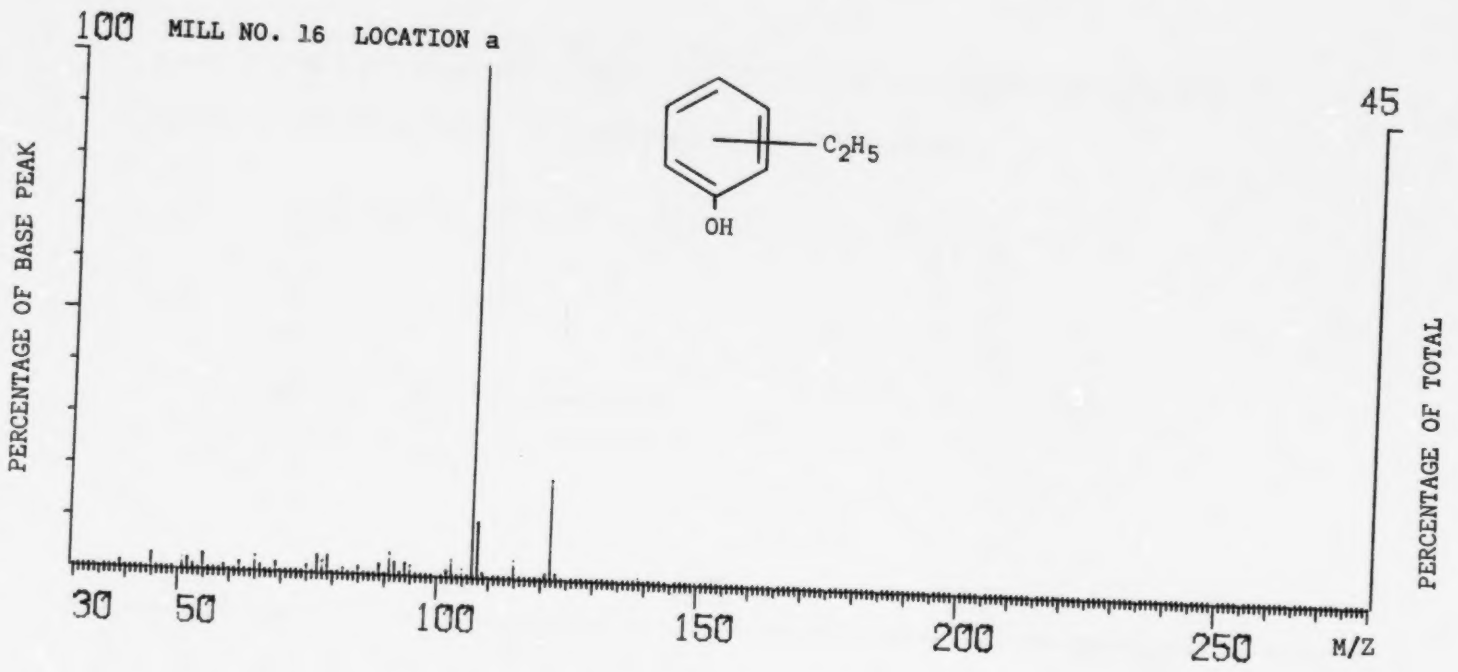
Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 2, Page 864.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	192	191	189	165	163	152
PERCENT OF BASE PEAK	100	66	31	15	4	3



Tentative Identification 1-METHYLBENZO-(c)-PHENANTHRENE

Safe, S. and O. Hutzinger. Mass Spectrometry of Pesticides and Pollutants. CRC Press, Cleveland, Ohio, 220 p. (1973).

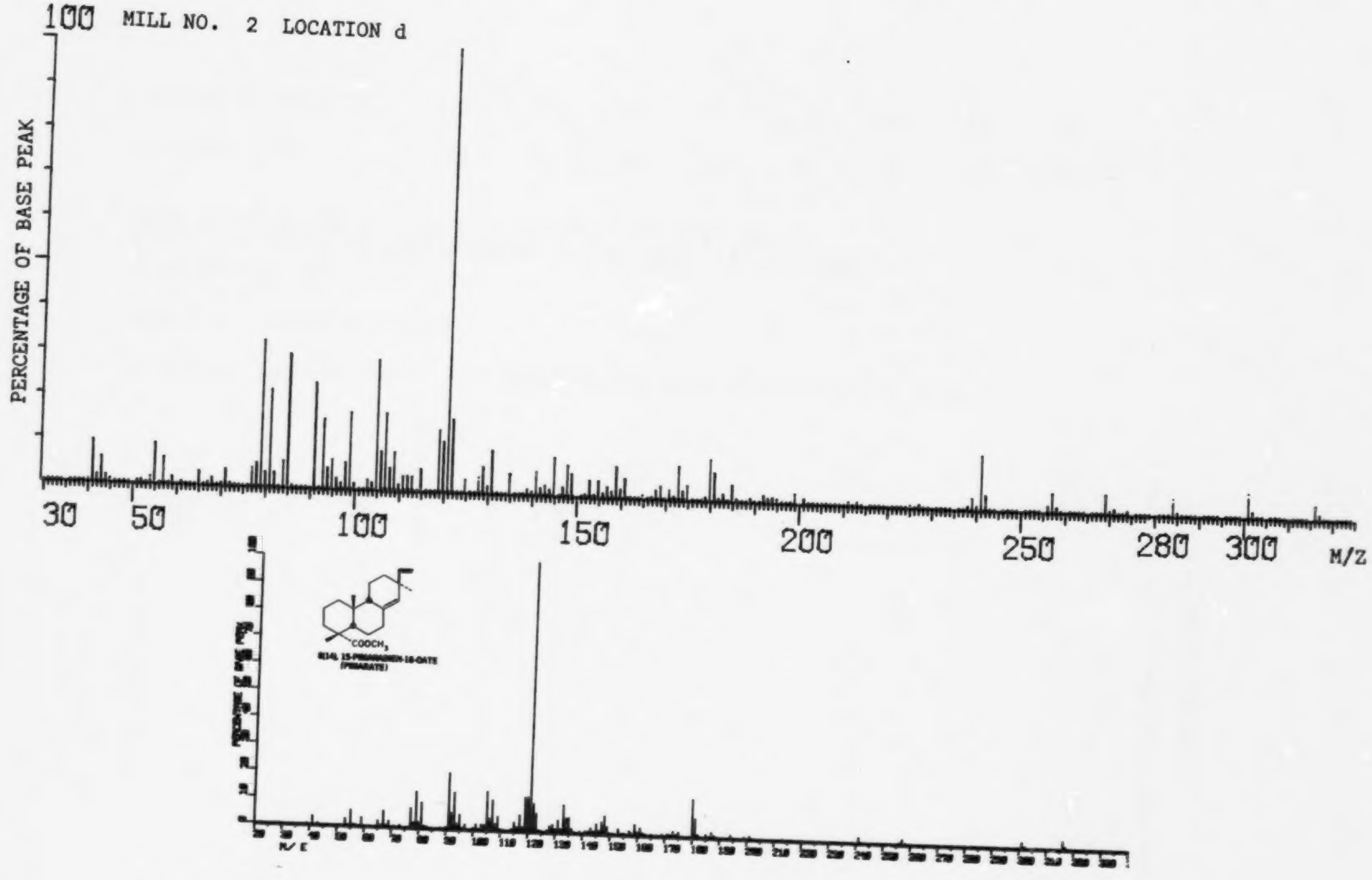


Tentative Identification ETHYL PHENOL

Based on Tabular Data From:

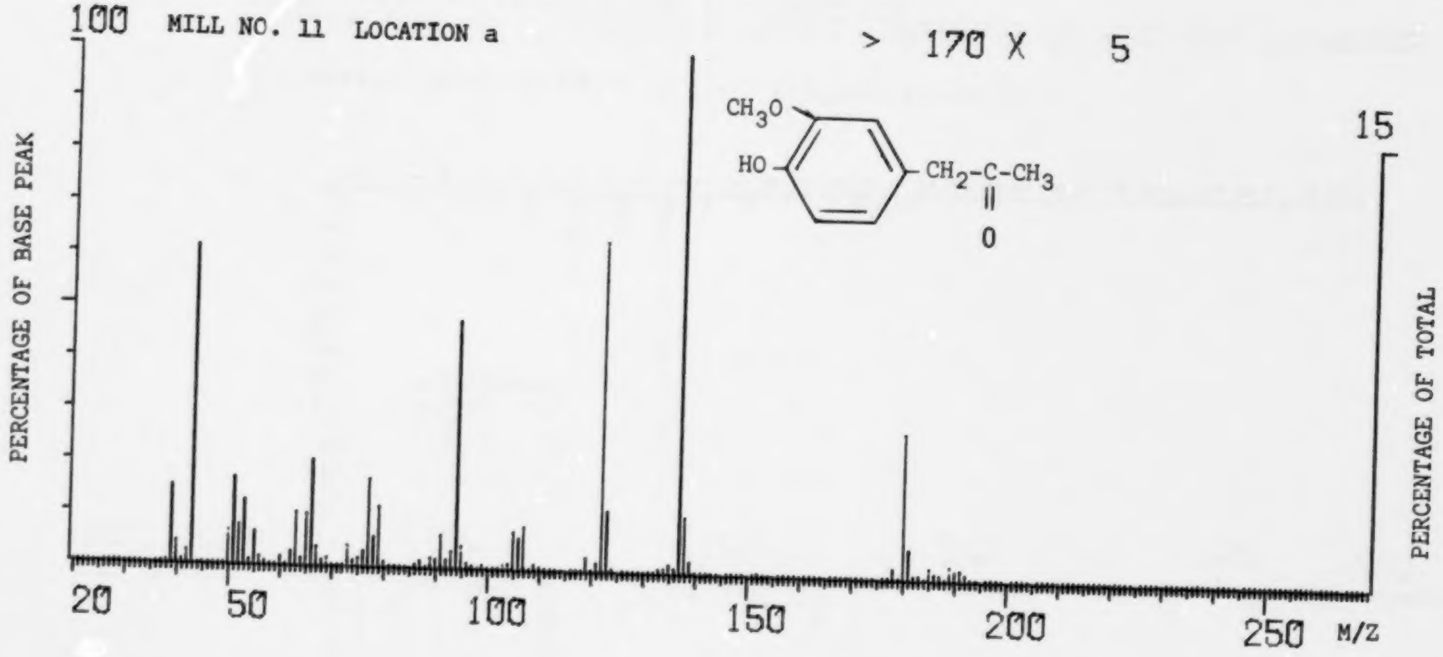
Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 3, Page 2094.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	107	122	77	108	39	121	91	51
PERCENT OF BASE PEAK	100	32	12	8	4	3	3	3



Tentative Identification 8,(14),15-PIMARADIEN-18-OATE

Keith, L.H. (Ed.). Analysis of Organic Compounds in Two Kraft Mill Wastewaters, EPA Report No. 660/4-75-005, 99 p. June (1975).

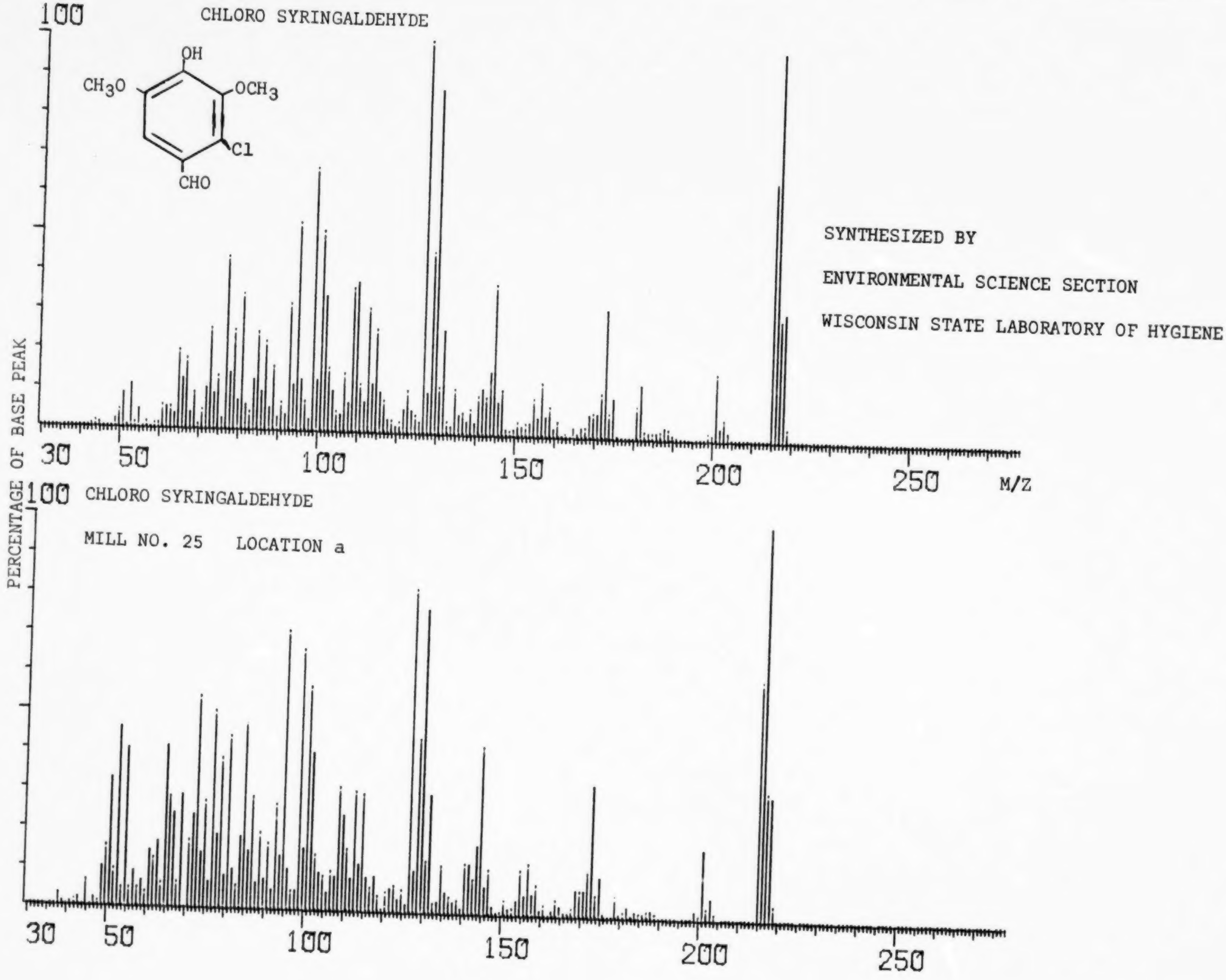


Tentative Identification 1-(4-HYDROXY-3-METHYL-PHENYL)-PROPAN-2-ONE

Based on Tabular Data From:

Mass Spectrometry Data Centre.
Eight Peak Index of Mass Spectra. 2nd ed. Vol. 3, Page 2297.
Mass Spectrometry Data Centre, Aldermaston, U.K. (1974).

FRAGMENT IONS	137	43	180	122	94	39	51	138
PERCENT OF BASE PEAK	100	49	29	22	21	19	19	16


CHLORO SYRINGALDEHYDE

SYNTHESIZED BY
ENVIRONMENTAL SCIENCE SECTION
WISCONSIN STATE LABORATORY OF HYGIENE

CHLORO SYRINGALDEHYDE

MILL NO. 25 LOCATION a

APPENDIX F

MASS SPECTRA OF COMPOUNDS NOT IDENTIFIED

Appendix F contains mass spectra of several unidentified compounds. Included are two similar non-chlorinated compounds with an apparent molecular weight of 196 (page F-4 and F-5). These two apparent isomers were often present when other chloro-organic compounds having one to three chlorines with apparent molecular weights of 230 (pages F-6, 7, 8, and 9), 264 (pages F-10, 11, and 12) and 298 (pages F-13 and 14) were found. Mass spectra reported by Fetizon et al. (40) suggest the non-chlorinated compounds might be diphenylacetaldehyde, trans-stilbene oxide, or a related compound. Additional mass spectra included in this appendix show apparent compounds with molecular weights of 290 (page F-15), 324 (page F-16), 358 (page F-18) and 392 (page F-19). These might be chloro-bisphenol A dimethyl ethers which eluted in a methylated acidic fraction of Mill 2 (page F-3). Compared with the spectra in Appendix D (page D-10) for bisphenol A dimethyl ether, the spectra of the chlorinated compounds have base peaks and apparent molecular ions shifted 34 mass units higher for each additional chlorine.

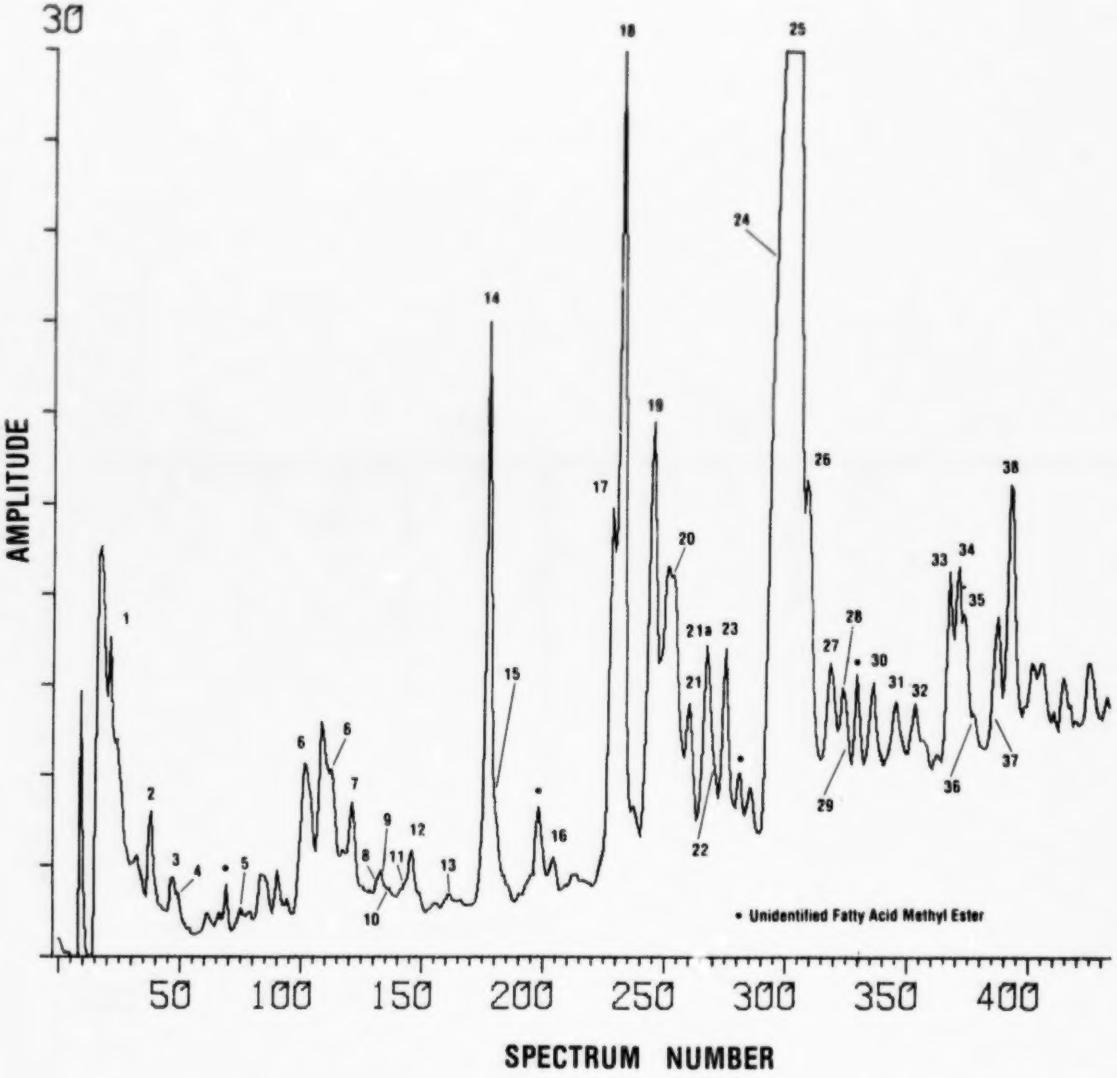
The mass spectrum in this appendix (page F-20), which has the isotopic clusters for three chlorine atoms with apparent isotopic molecular ions at m/z 270, 272 and 274, might represent trichloro-trimethoxy benzene. Before methylation, the spectrum for this compound was not detected. Instead, a later-eluting compound with apparent isotopic molecular ions m/z 256, 258 and 260 was detected, suggesting trichloro-dimethoxy phenol which is a more polar compound. By comparing the mass spectrum in this appendix (page F-20) with that of 3, 4, 5 trichloroveratrole in Appendix D (page D-25), the same initial losses of M-15, M-43 and M-58 are apparent.

Additionally, this compound eluted just after trichloroveratrole in the same methylated acidic fraction of Mill 2 (page F-3).

Also included in this appendix are two isomers of an apparent resin acid methyl ester (page F-21 and 22) and a possibly related chlorinated compound (page F-23). The mass spectra of these two apparent isomers are virtually identical, having an apparent molecular ion of m/z 328 and losses of M-15 and M-75. These two compounds are also very similar to methyl-oxo-dehydroabietate listed in Appendix E (page E-10), except the fragment ions m/z 259 and 296 are missing from them. Ion m/z 259 is consistent for the loss of the carbomethoxy group ($COOCH_3^{\cdot}$). Ion m/z 296 appears to indicate a loss of 17 ($OH^{\cdot}$) from m/z 313 which is the $(M-CH_3^{\cdot})^+$ fragment. Since the two compounds eluted much earlier than methyl-oxo-dehydroabietate but soon after methyl dehydroabietate, we hypothesize they might represent ethyl dehydroabietate, which would also have a molecular weight of 328. This hypothesis remains unproven at the present time.

TOTAL ION CHROMATOGRAM : METHYLATED ACID EXTRACT OF A PAPER MILL EFFLUENT

Column Conditions: Ultra-Bond 20M, 3m x 2mm,
temperature programmed 110-250°C @ 4°C/min. for 35 minutes



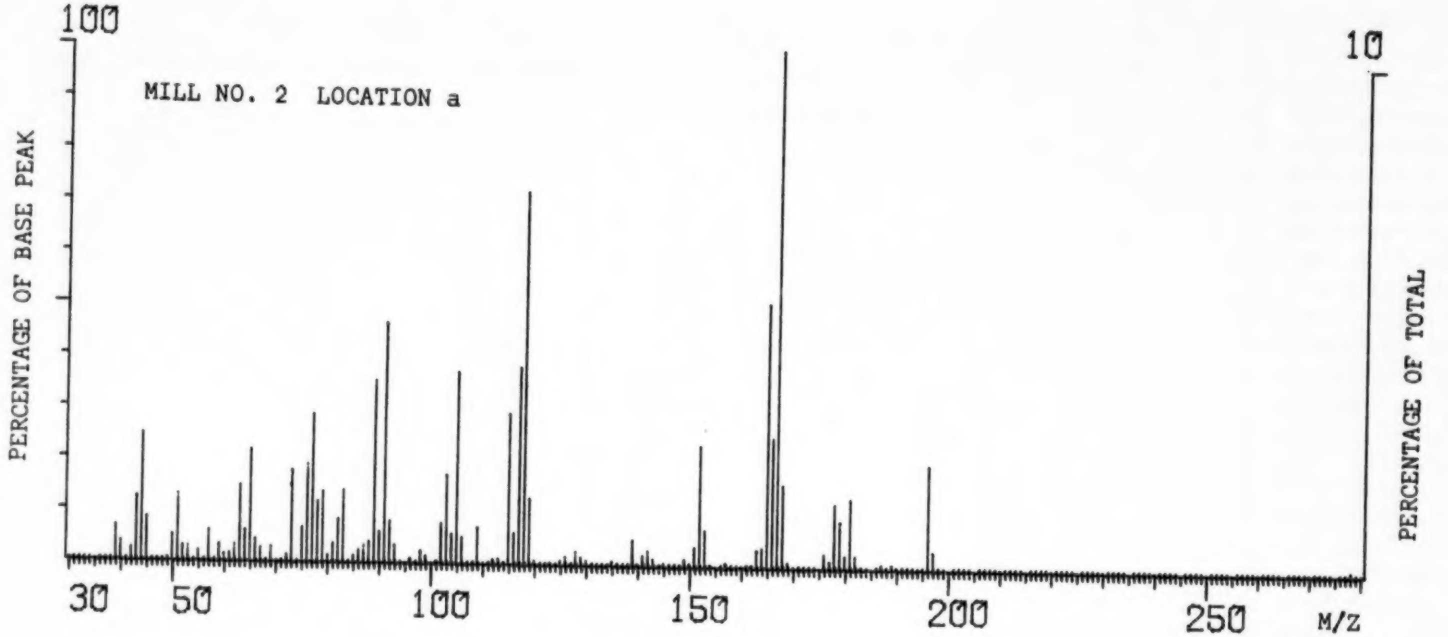
COMPOUNDS

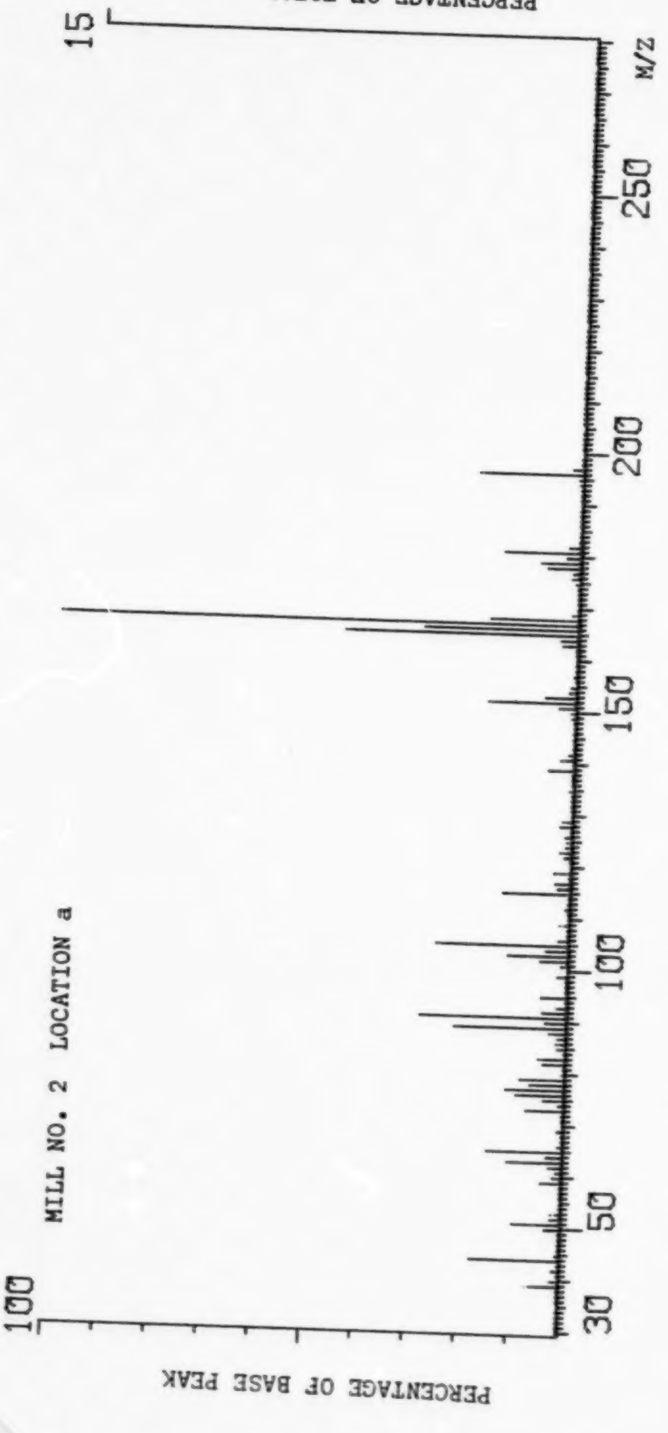
1. Chloroanisole
2. 2, 4, 6 - Trichloroanisole
3. Dichloroanisole
4. Benzothiazole
5. Tetrachloroanisole
6. Nonyl anisole
7. Pentachloroanisole
8. Tetrachloroveratrole
9. Methyl thiobenzothiazole
10. Trichloroveratrole
11. Trichloro-trimethoxybenzene
12. Tributyl phosphate
13. Methoxybenzothiazole
14. Methyl palmitate
15. Aldrin — External standard
16. Methyl heptadecanoate
17. Methyl oleate
18. Methyl stearate
19. Methyl 8, 15 - isopimardien-18-oate
20. Methyl pimarate
21. Methyl sandaracopimarate

21 a. Bisphenol a dimethyl ether

22. Unidentified R A M E* (MW 318)
23. Unidentified R A M E (MW 316)
24. Unidentified R A M E (MW 328)
25. Methyl dehydroabietate
26. Methyl 6, 8, 11, 13-abietatetraen-18-oate
27. Unidentified R A M E (MW 328)
28. Dichloro-bisphenol a dimethyl ether
29. Chloro-bisphenol a dimethyl ether
30. Chloro R A M E (MW 362)
31. Chloro-methyl dehydroabietate (A)
32. Chloro-methyl dehydroabietate (B)
33. Tetrachloro-bisphenol a dimethyl ether
34. Dioctyl phthalate
35. Trichloro-bisphenol a dimethyl ether
36. Dichloro-bisphenol a dimethyl ether
37. Dichloro-methyl dehydroabietate (MW 382)
38. Methyl oxo-dehydroabietate (MW 328)

*R A M E = Resin Acid Methyl Ester


100
MILL NO. 2 LOCATION a
PERCENTAGE OF BASE PEAK
10
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z



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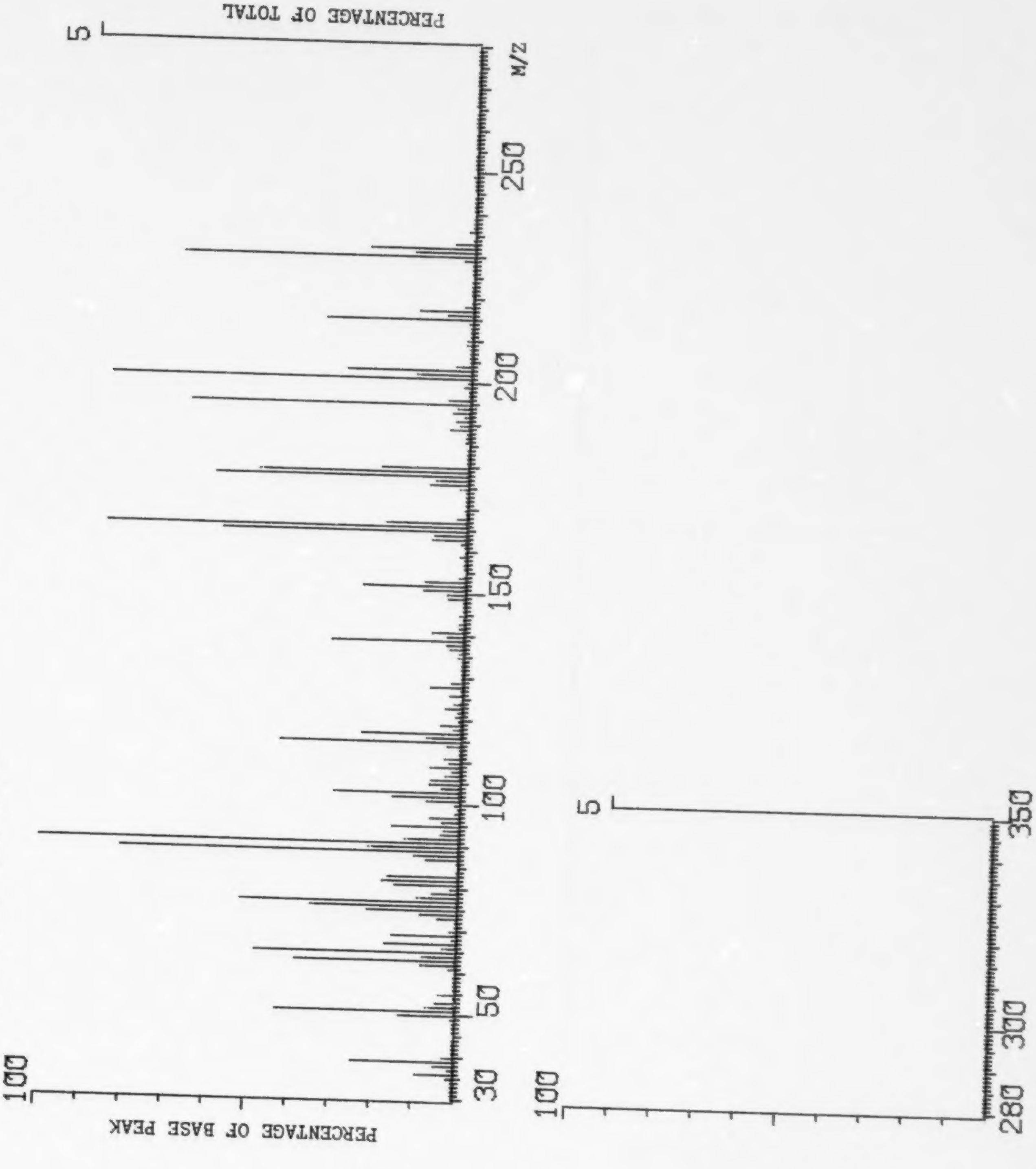
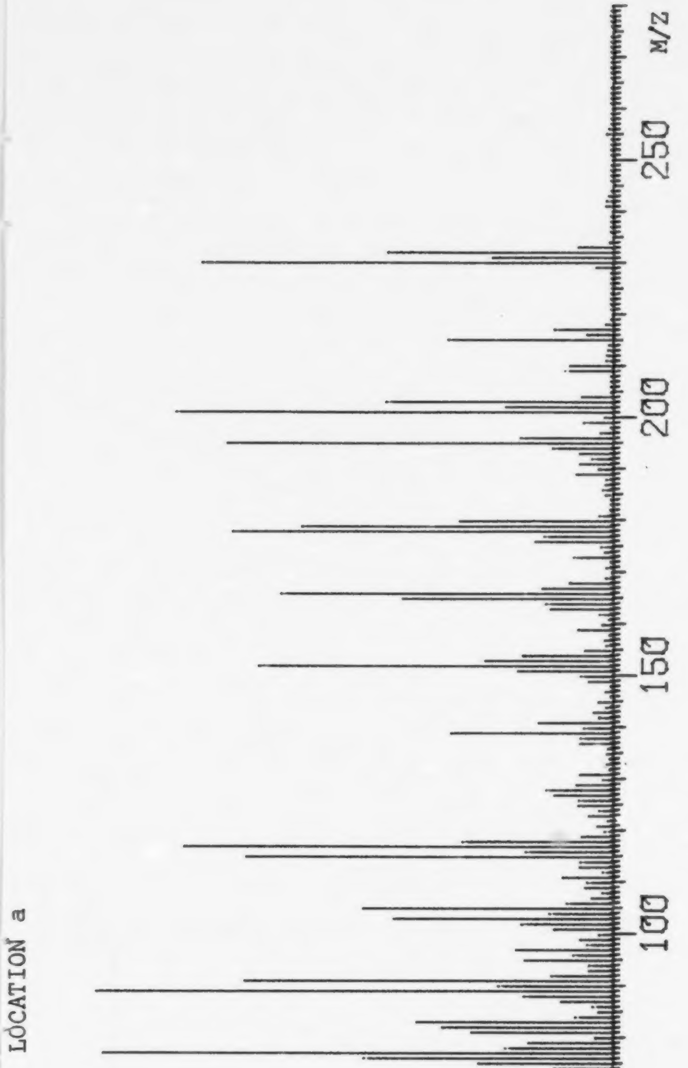
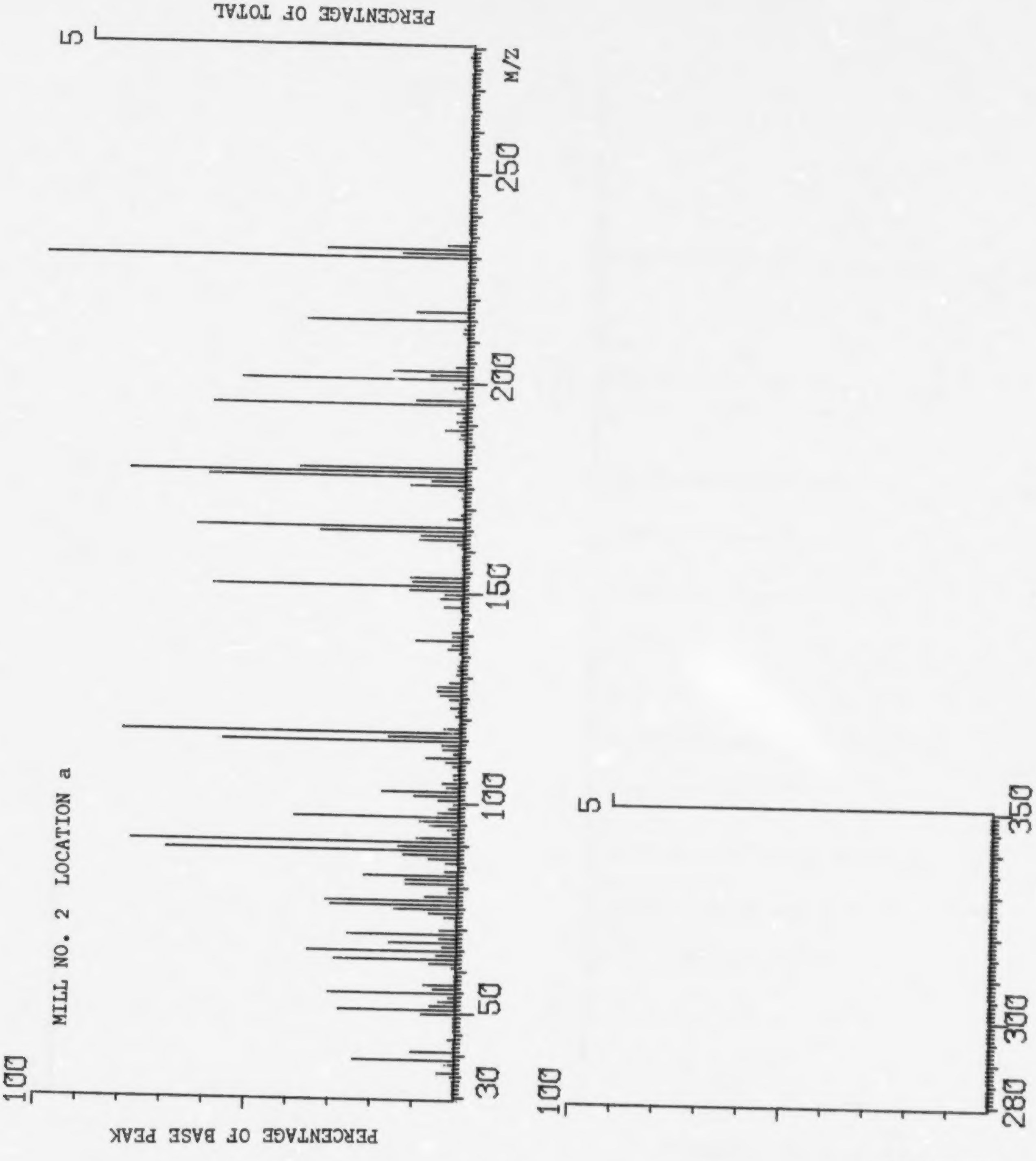


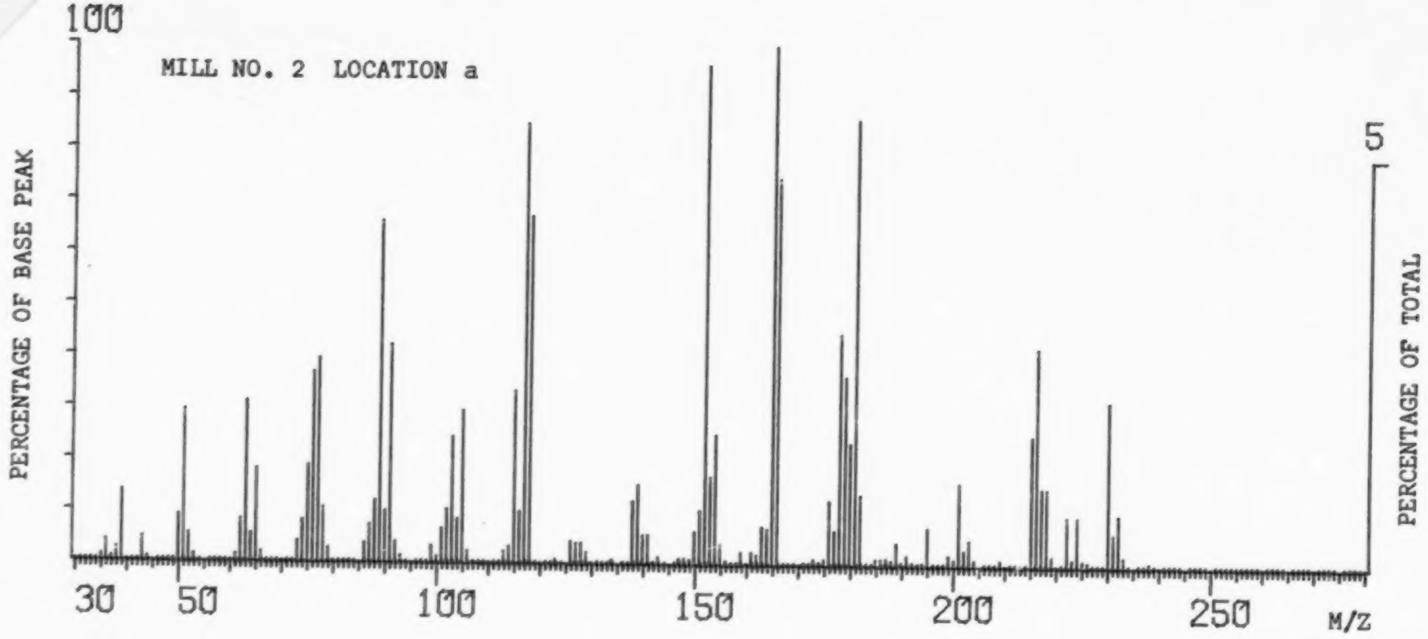
MILL NO. 2 LOCATION a

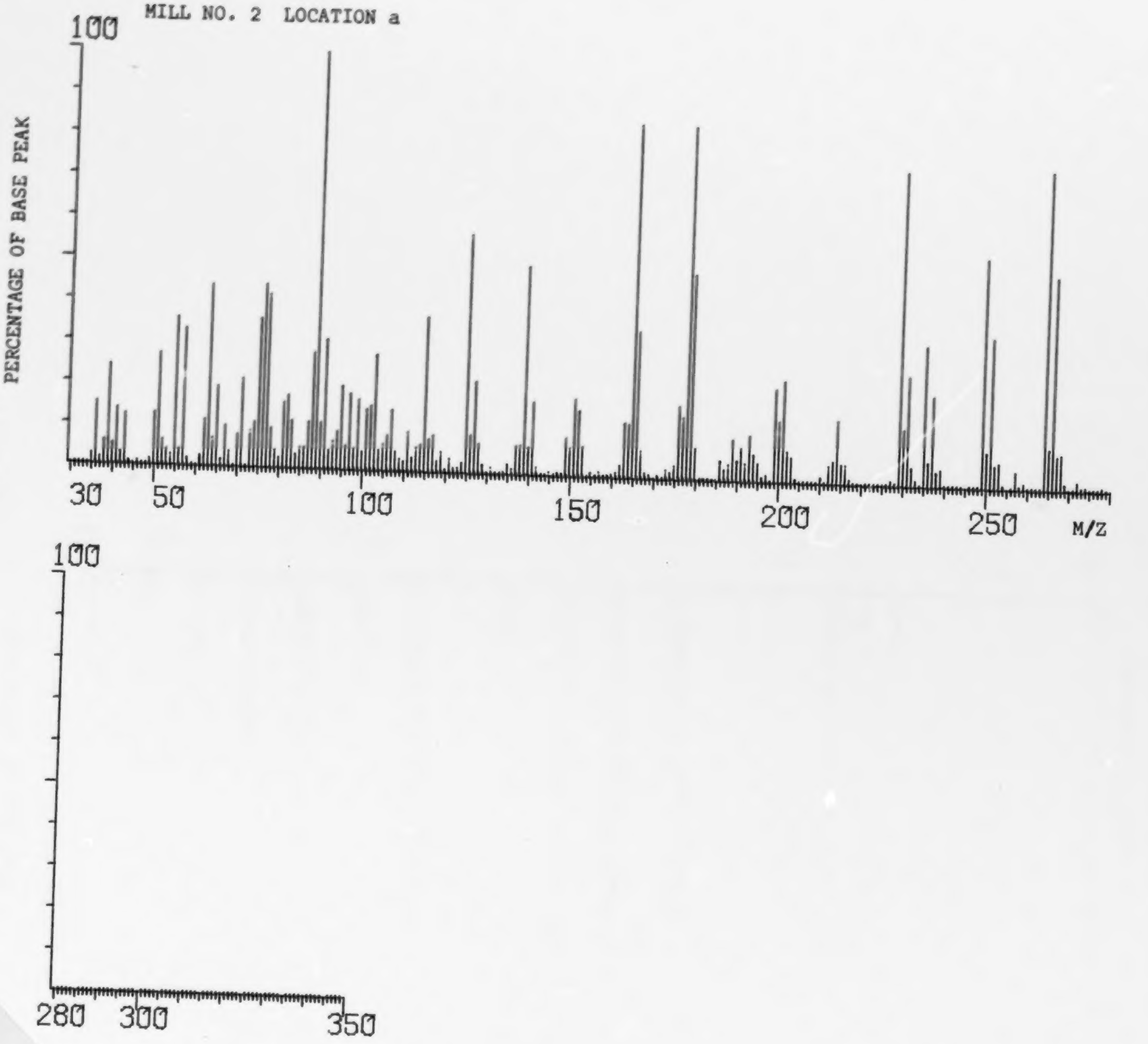

MILL NO. 2 LOCATION a
100
PERCENTAGE OF BASE PEAK
30
50
100
150
200
250
M/Z
100
280
300
350

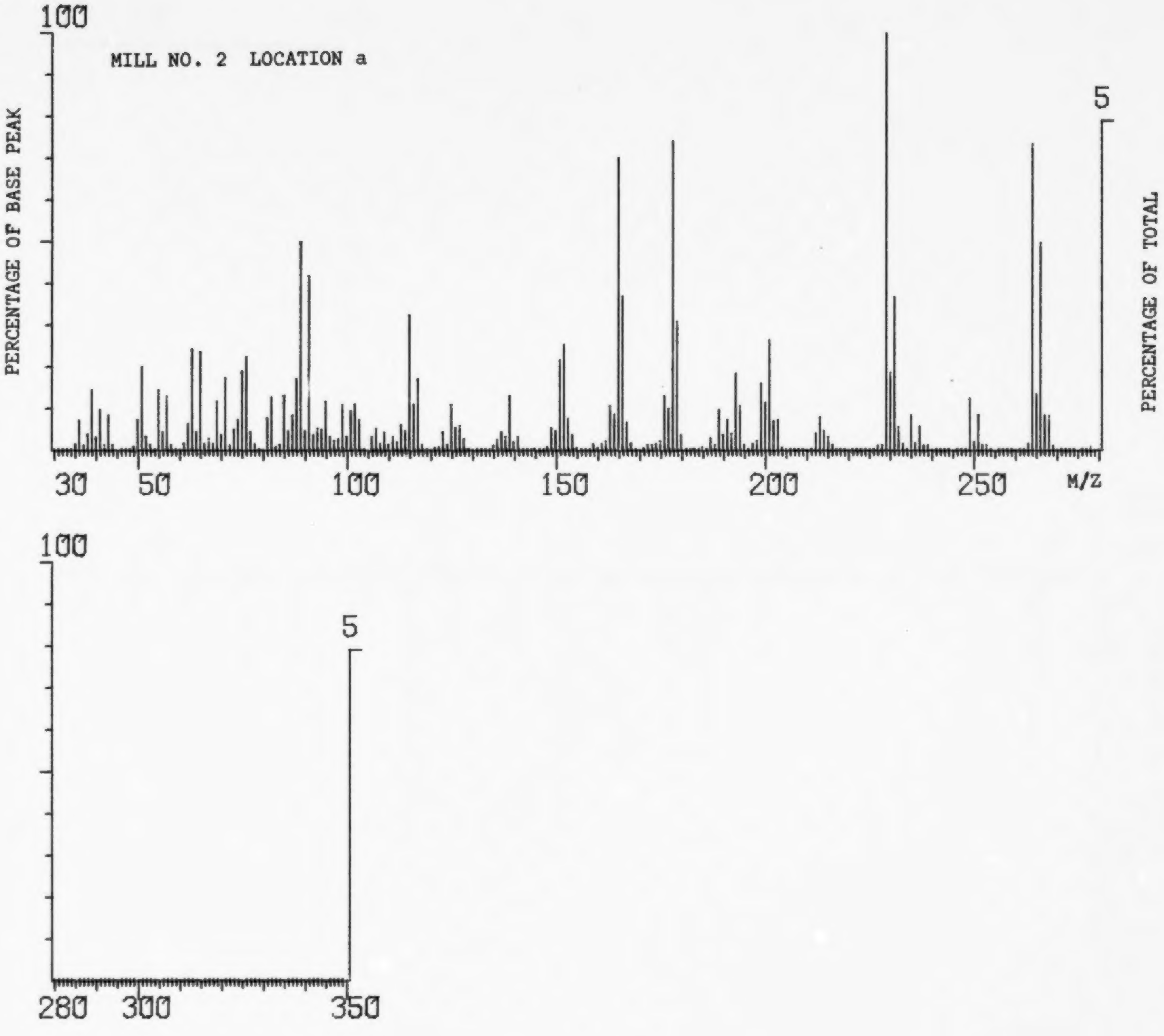


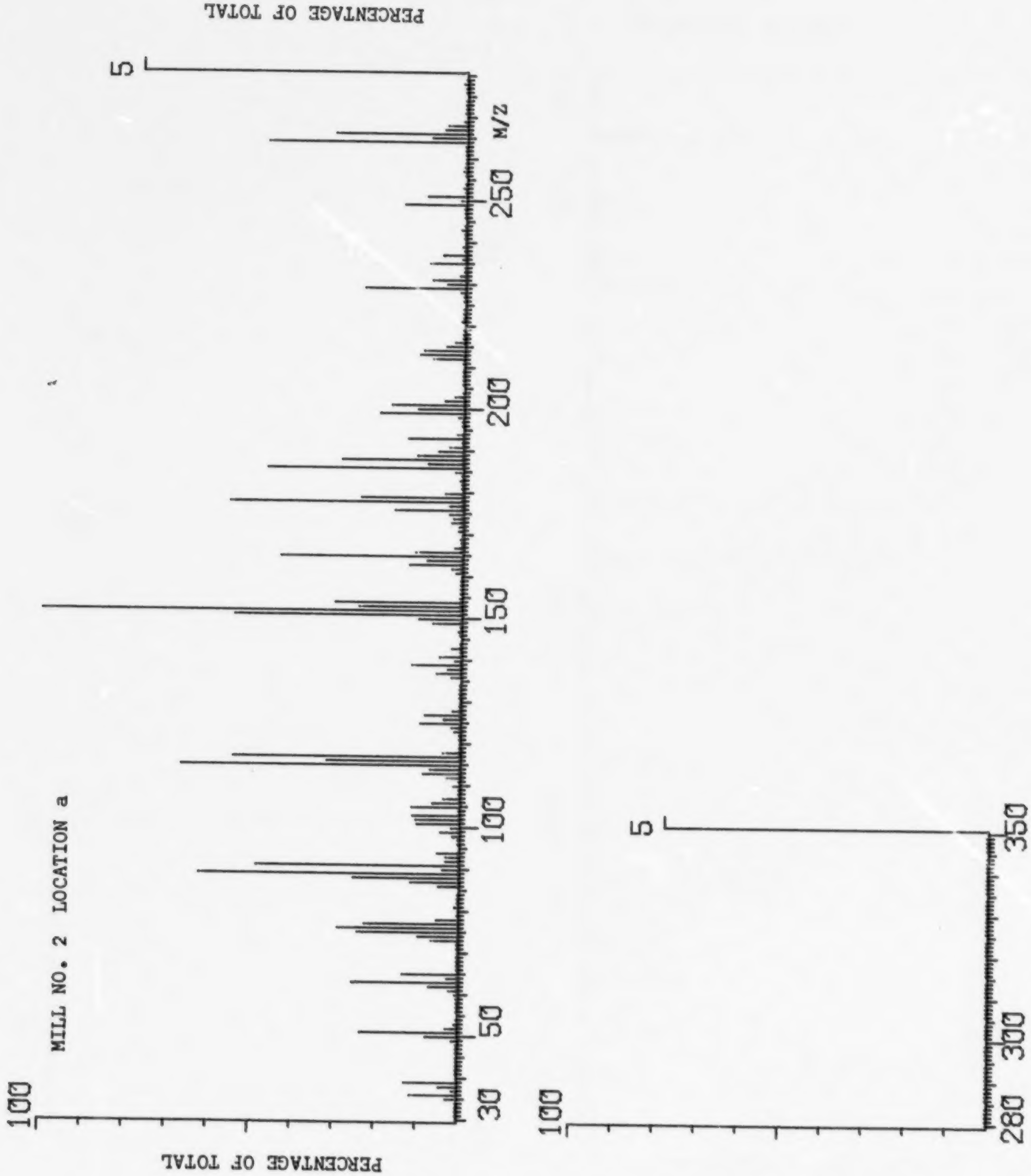
MILL NO. 2 LOCATION a

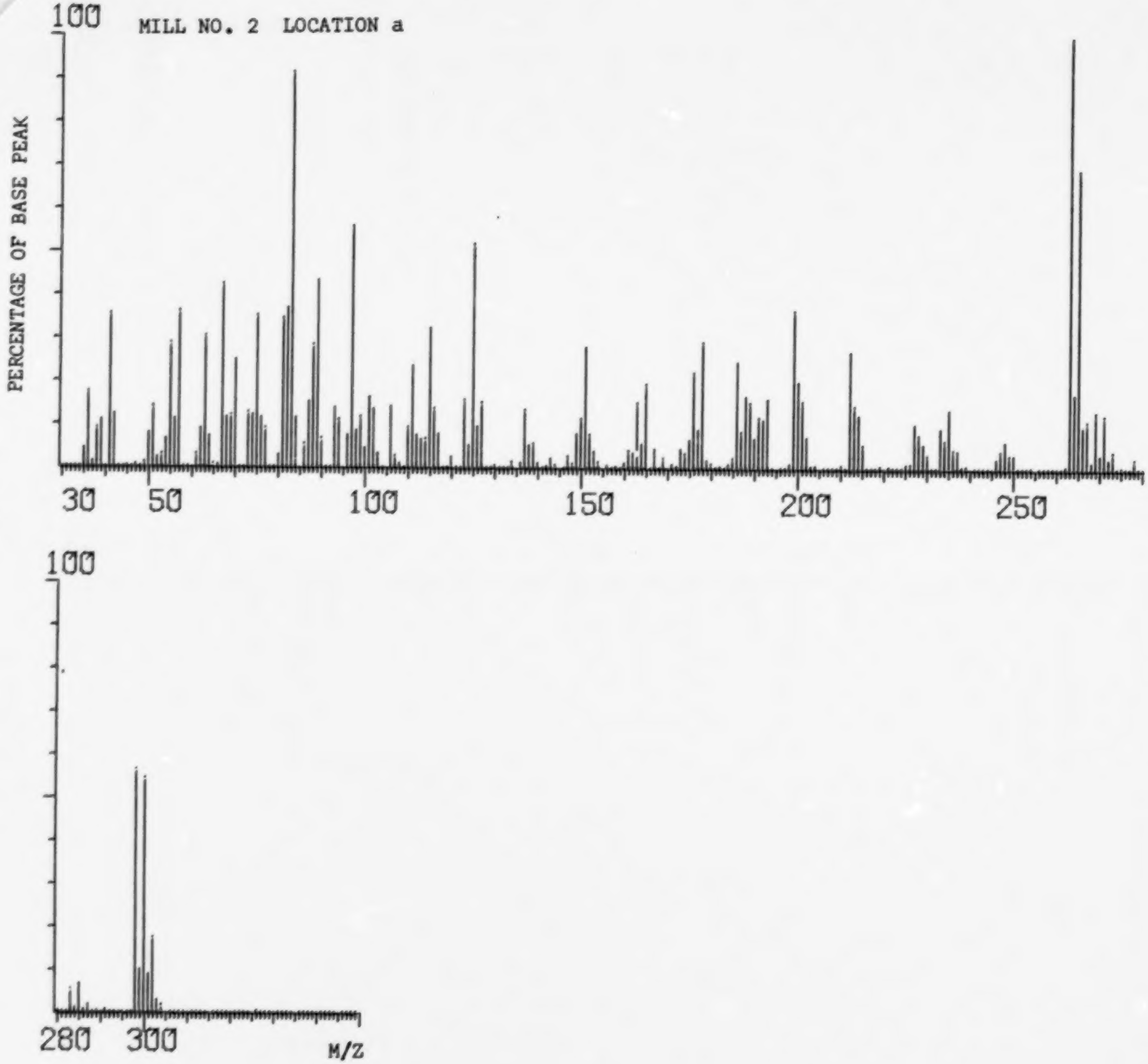
GPO 821-649-16


100
MILL NO. 2 LOCATION a
PERCENTAGE OF BASE PEAK
5
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z


MILL NO. 2 LOCATION a
100
PERCENTAGE OF BASE PEAK
30
50
100
150
200
250
M/Z
100
280
300
350

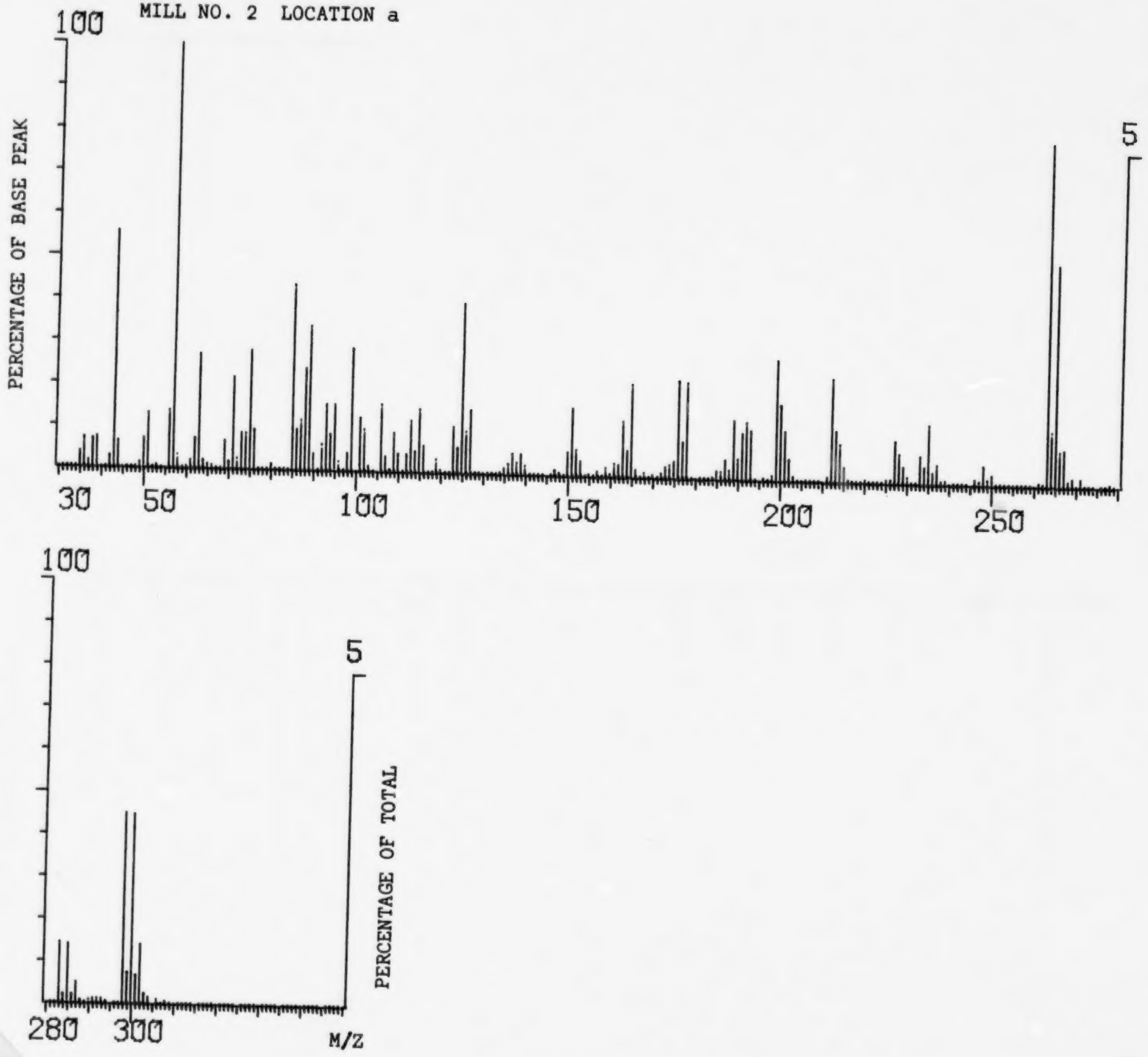

MILL NO. 2 LOCATION a
100
5
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL
30
50
100
150
200
250
M/Z
100
5
280
300
350

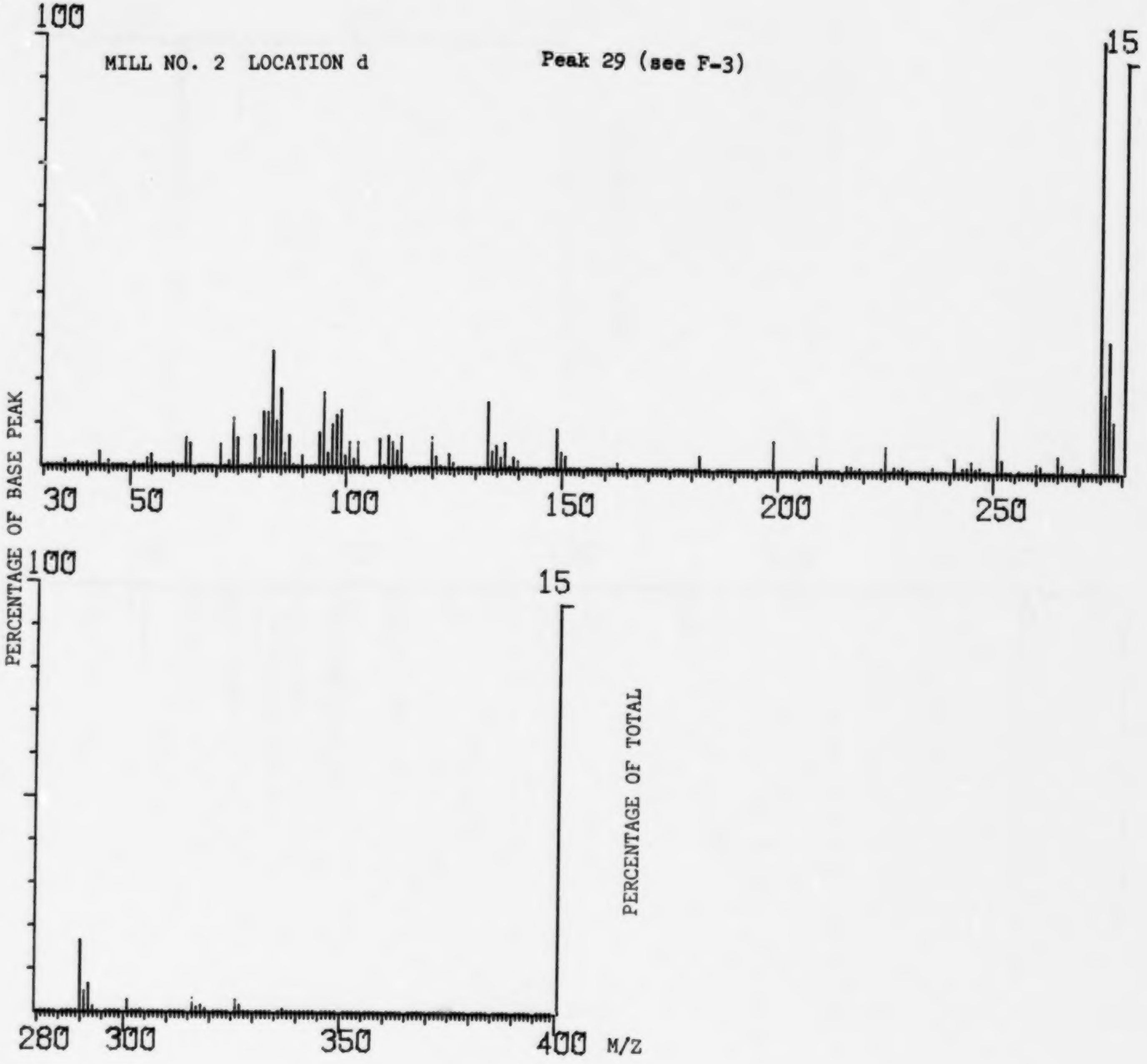

MILL NO. 2 LOCATION a
PERCENTAGE OF TOTAL
100
5
M/Z
30
50
100
150
200
250
280
300
350

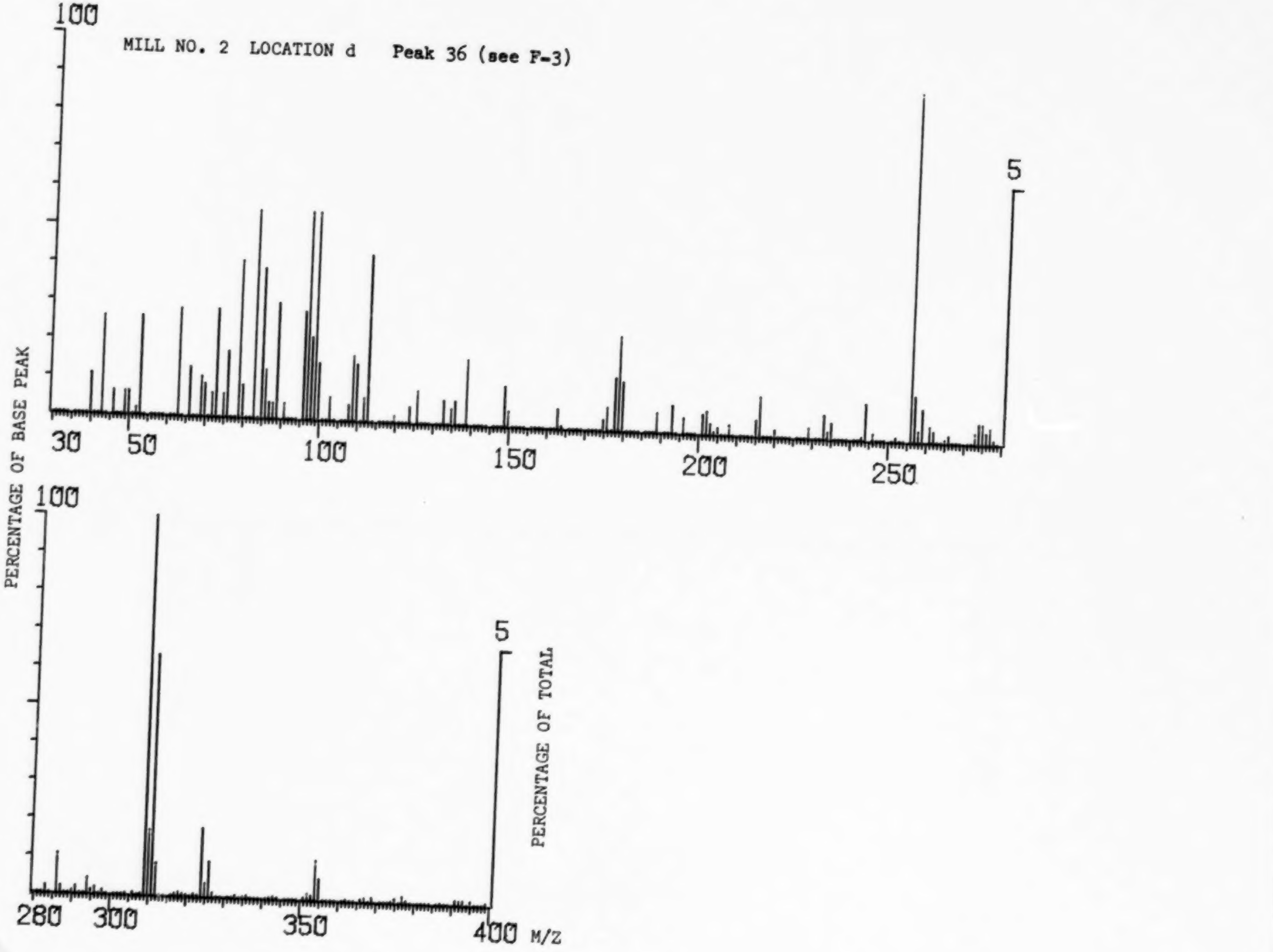


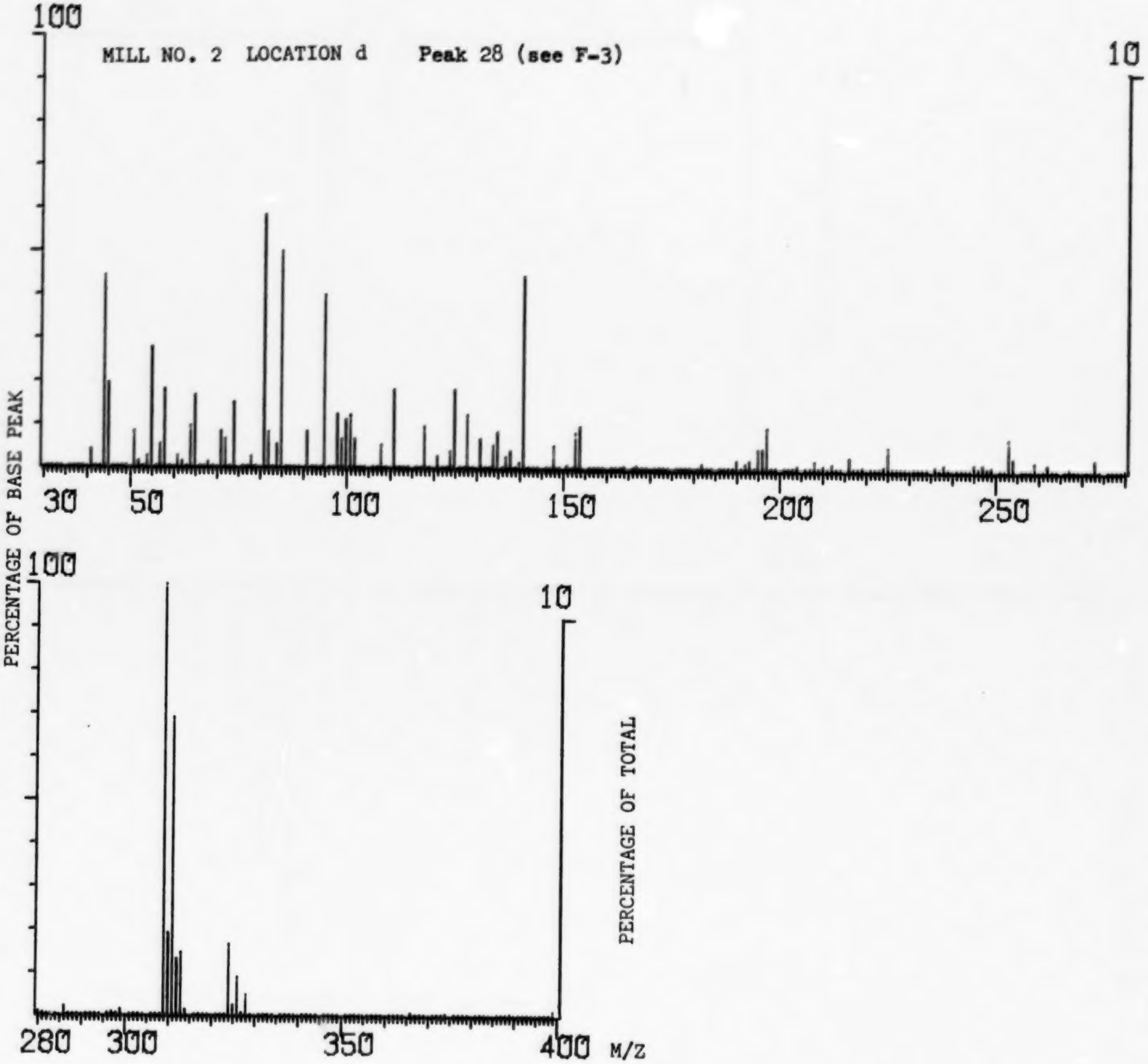
MILL NO. 2 LOCATION a

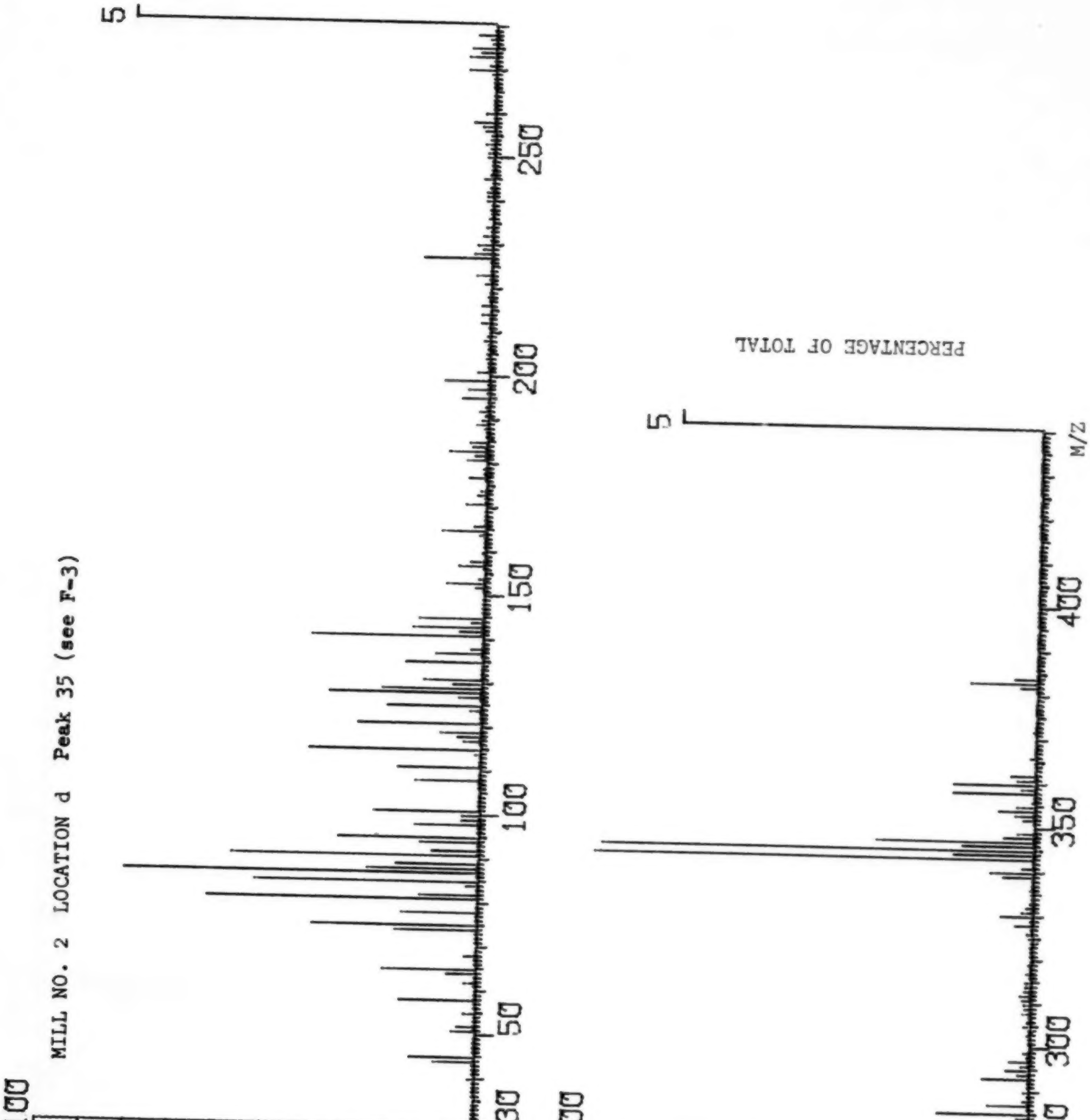
MILL NO. 2 LOCATION a

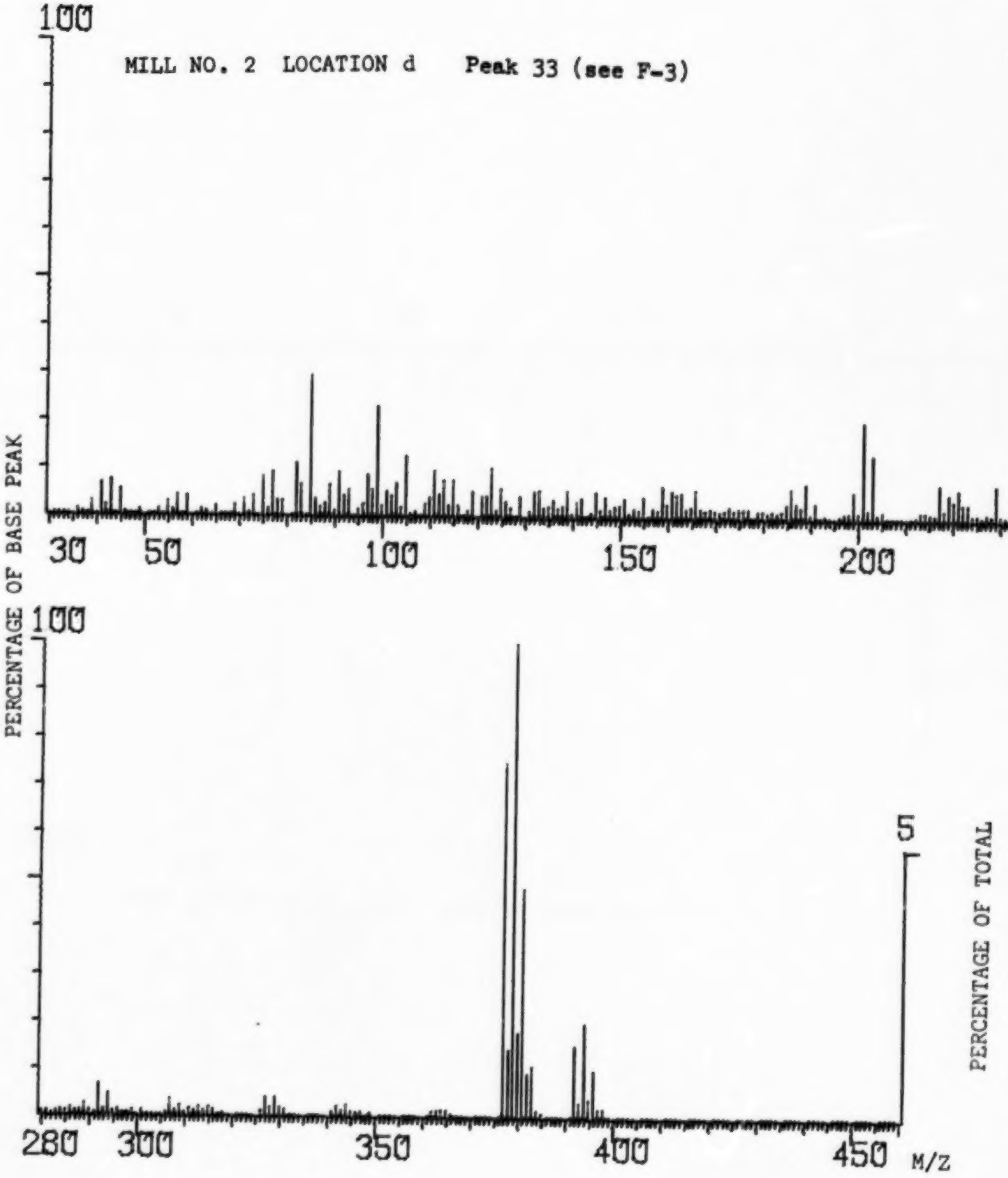



MILL NO. 2 LOCATION d
Peak 29 (see F-3)
100
15
PERCENTAGE OF BASE PEAK
30
50
100
150
200
250
100
15
PERCENTAGE OF TOTAL
280
300
350
400
M/Z

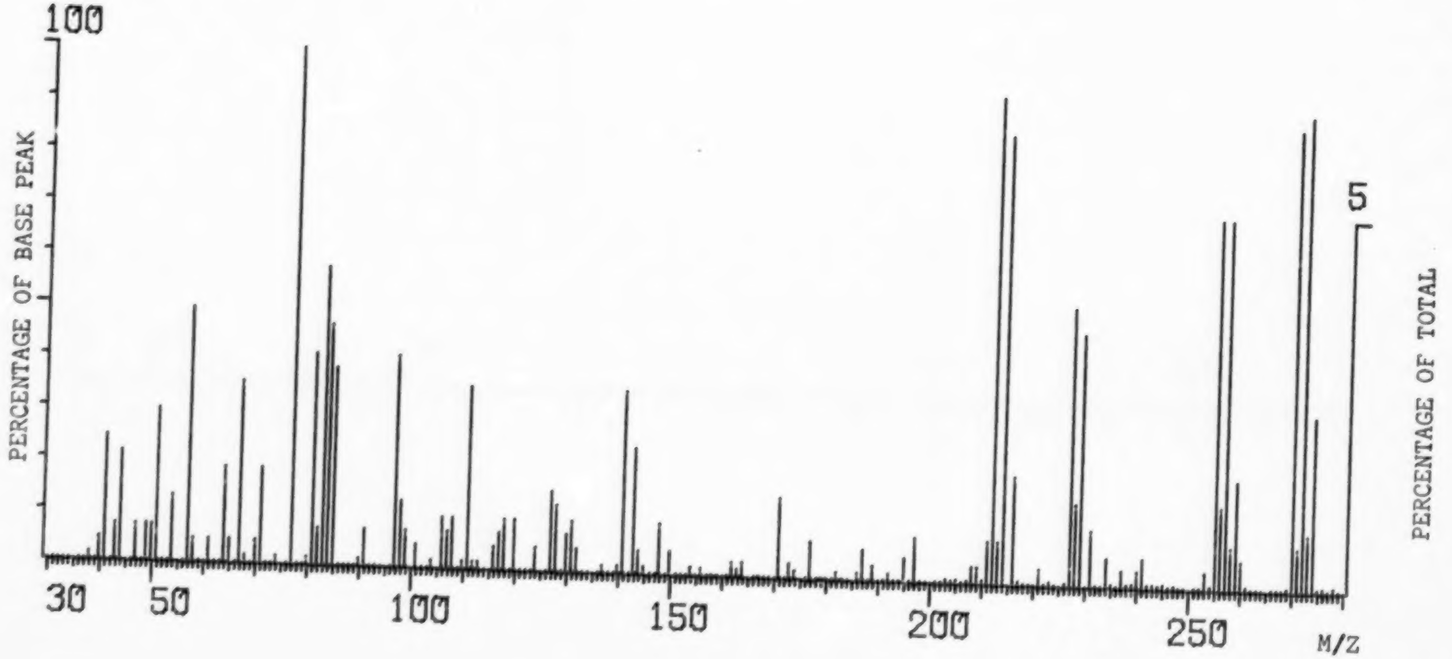

MILL NO. 2 LOCATION d **Peak 36 (see F-3)**

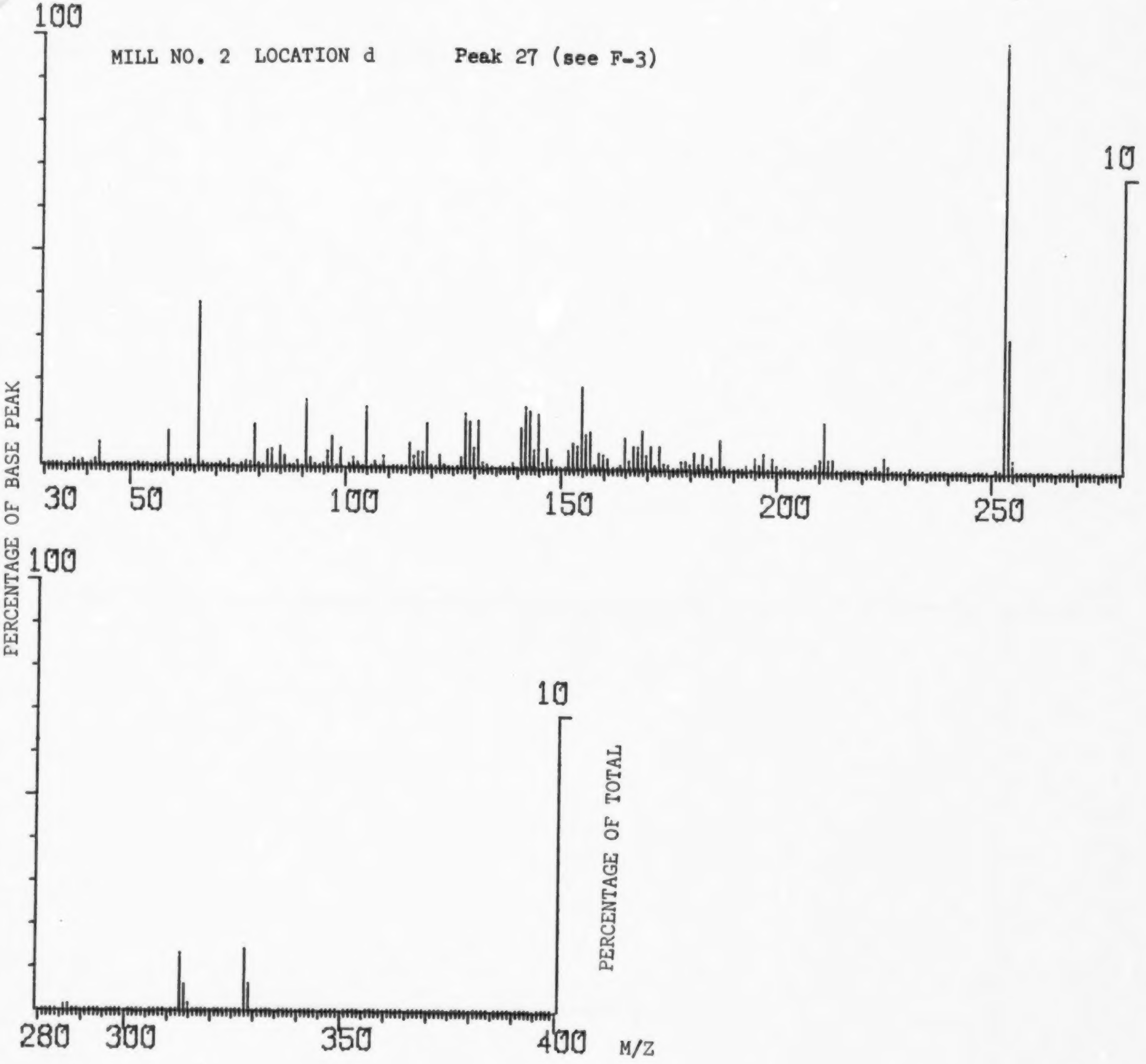

MILL NO. 2 LOCATION d **Peak 28 (see F-3)**


MILL NO. 2 LOCATION d Peak 35 (see F-3)
100
5
30
50
100
150
200
250
100
5
280
300
350
400
M/Z
PERCENTAGE OF BASE PEAK
PERCENTAGE OF TOTAL

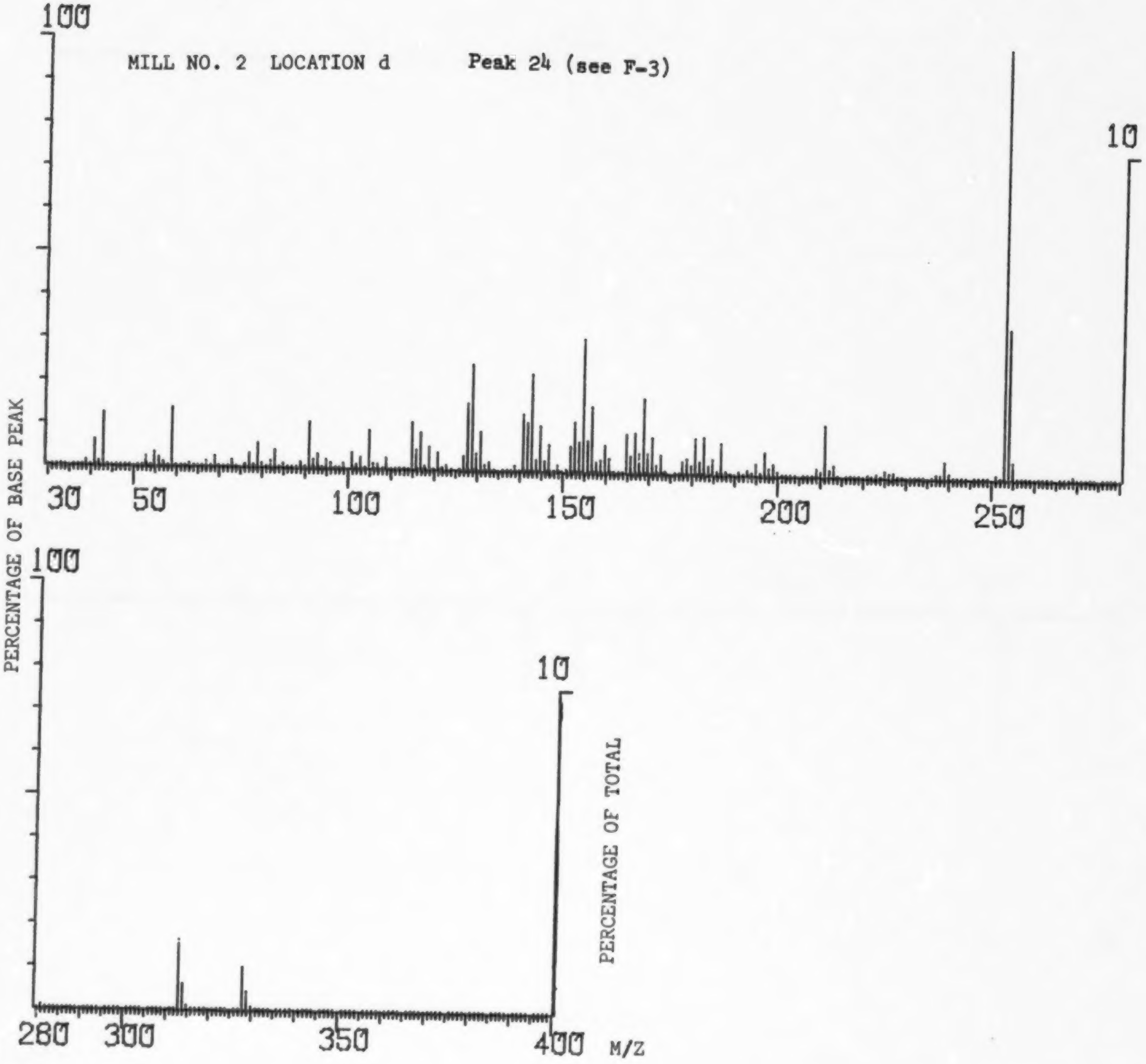

MILL NO. 2 LOCATION d   Peak 33 (see F-3)

MILL NO. 2 LOCATION d **Peak 11** (see F-3)





MILL NO. 2 LOCATION d **Peak 27 (see F-3)**



MILL NO. 2 LOCATION d Peak 24 (see F-3)

MILL NO. 2 LOCATION d **Peak 30 (see F-3)**